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DISPOSAL AND UTILIZATION OF WASTE KILN
DUST FROM CEMENT INDUSTRY

Thomas A. Davis, et al

Southern Research Institute

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Project No. R-801872
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FOREWORD

Man and his environment must be protected from the adverse effects of pesticides, radiation, noise and other forms of pollution, and the unwise management of solid waste. Efforts to protect the environment require a focus that recognizes the interplay between the components of our physical environment--air, water, and land. The National Environmental Research Centers provide this multidisciplinary focus through programs engaged in

- studies on the effects of environmental contaminants on man and the biosphere, and
- a search for ways to prevent contamination and to recycle valuable sources.

The studies for this report were undertaken to determine the nature, quantity and fate of dust collected from the effluent gases of cement kilns, to identify and describe potential uses for the dust, and to identify specific areas where the Agency's participation in the development of new technology could have maximum effect on the cement industry's efforts to protect our Nation's environment.

A. W. Breidenbach, Ph.D.
Director
National Environmental
Research Center, Cincinnati

ABSTRACT

A survey that included 60% of the cement manufacturing plants in the United States was made to determine the fate of dust collected from the gases emanating from cement kilns. Because of high alkali content, large quantities of the dust cannot be returned to the cement-making process. A survey was made of the literature in the United States and Europe pertaining to handling, reclaiming, and utilizing the collected dust. Abstracts of 71 references are included in the Appendix. Acid neutralization capacity and potash content make the dust valuable for application to farmland, and the potential market for agricultural use alone could consume all of the waste dust that is now being discarded.

This report was submitted by Southern Research Institute in fulfillment of Project No. R-801872 under the sponsorship of the Environmental Protection Agency.

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We acknowledge the aid of Mr. George A. Wieczorek of the Division of Chemical Development, Tennessee Valley Authority, in providing considerable information concerning the use of cement dust for fertilizer, and of Dr. Robert C. Rund, Secretary of the Association of American Plant Food Control Officers, for providing information on specifications for fertilizer materials.

Dr. Charles E. Feazel, Senior Research Advisor, Southern Research Institute, assisted in our literature survey by translating a number of patents and journal articles that were available only in German or Russian. He also assisted in editing this report.

SECTION I

CONCLUSIONS

The exhaust gases from portland cement kilns carry away an average of 12.2% of the kiln feed. To reduce particulate emissions, an average of 96% of this material is removed from the exhaust gases by dust collectors. Since the dust has an estimated value of \$2 per ton, it is returned to the kiln whenever possible. Of the 16.4 million tons of dust collected annually from cement kiln exhausts, 11.9 million tons are returned to the cement-making process, and 4.5 million tons are discarded.

The major factor preventing return of more dust to the kilns is that the high concentration of alkalies in the dust would cause the alkali content of the clinker to exceed the limit of 0.6%. Seven plants employ a leaching process to remove the alkalies so that the dust can be returned, but the alkalies in the leachate pose a serious water pollution problem. Several other techniques for removing alkalies are described in the literature, but none is presently used in the United States.

Most waste kiln dust is stored in open piles on the ground or in abandoned quarries. The highly alkaline runoff of rainwater from disposal sites can cause pollution of streams or ground water unless it is contained and treated. The combined costs of hauling the dust and controlling runoff appear to make dust disposal economically and ecologically unattractive. In most cases cement manufacturers would give away their waste dust if someone would take it.

The markets for agricultural lime and potash fertilizer materials are large enough to consume all of the waste kiln dust that is currently being discarded. Moreover, on the basis of numerous studies cited in this report, the chemical composition of kiln dust appears suitable for the dust to be applied to acidic soils and to soils that require additional potassium. However, only small amounts of the dust are being used for this purpose in the United States.

Other uses for waste dust from cement kilns include landfill, soil stabilization, neutralization of acidic wastes (e.g. mine drainage and pickle liquor), absorption of SO₂ from stack gases, water treatment, glass making, and production of light-weight aggregate.

SECTION II

RECOMMENDATIONS

This state-of-the-art study was limited to a survey of the industry to determine present practice of dust disposal and utilization and a survey of the literature to identify potential alternatives to wasting high-alkali kiln dust. It was not within the scope of the program to perform demonstration experiments or to establish the economic feasibility of various alternatives for dust utilization.

Since agricultural uses appear to be the most promising applications of dust that cannot be returned to the cement-making process, we recommend that action be initiated with the Association of American Plant Food Control Officials (AAPFCO) to have cement dust specified as an agricultural liming material and as a potassium fertilizer material. The data obtained in our survey concerning the quality and quantity of dust available from cement plants could be used by the AAPFCO to establish specifications that might allow the dust to be applied to farmlands without any modifications of its properties. Specifications that require little or no monitoring and control of the composition of the material would facilitate distribution and marketing of the dust by the cement manufacturers. On the other hand, AAPFCO may determine that modifications of the chemical composition and physical form of the dust would make it more suitable as a fertilizer material. This may require a research program to develop methods of treating the dust from various cement plants to meet the specifications.

The dust leaching systems presently in operation at seven plants appear to be economically attractive; however, substantial modifications to the leaching process will be required to meet water pollution control regulations. We recommend that studies be undertaken to determine the economic feasibility of recovering alkalies from the leachate so that they are not discharged to the environment. If alkali recovery appears justified, we recommend that pilot plant facilities be set up and operated with an existing leaching operation to demonstrate technical feasibility.

SECTION III

INTRODUCTION

The manufacture of portland cement is accompanied by the generation of large quantities of dust. Grinding and conveying raw materials, heating them in a rotary kiln, and grinding the resulting clinker are all dust-producing operations, and the dust escaping from these operations must be collected to prevent air pollution.¹ Dust collected in raw material processing operations can be returned to the process, and dust from clinker grinding can be sold as cement. Since the manufacturer has economic incentive to collect and reuse these dusts,² their disposal is seldom a problem, and they will not be discussed further in this report.

The dust generated in the rotary kiln is difficult to collect because it is entrained in large volumes of hot exhaust gases. Moreover, it often contains unacceptably high concentrations of alkalies (sodium and potassium) which make it unsuitable for return to the cement-making process. Disposal of the dust is complicated by the presence of soluble alkalies in the dust; when these are leached out by rainwater, they can cause pollution of surface or ground waters. This study was undertaken to assess the problems associated with kiln-dust disposal and to find and evaluate possible solutions to these problems with an emphasis on utilization of waste dust rather than development and maintenance of expensive and wasteful disposal systems.

A successful assessment of the state of the art of collection, disposal and utilization of waste kiln dust required a review of pertinent technical literature. Chemical Abstracts, the reference files of the Portland Cement Association and a bibliography from the Tennessee Valley Authority were used to gain initial access to the literature. The literature search yielded numerous references, both foreign and domestic, which were screened for their applicability to the purpose of the study. Polish, Russian, and German articles made up the bulk of the pertinent foreign literature. Whenever the title or published abstract of an article appeared relevant, the original article was copied and read. In several cases we corresponded with the author to update or elaborate on the information published in his article or patent. Many articles in foreign languages were translated by members of the staff of Southern Research Institute. Abstracts for references cited in this report are given in the Appendix.

Concurrent with this study, we were also engaged in a survey to obtain the background data necessary to establish the Effluent Limitation Guidelines for the Cement Industry. The data forms

used to record information from phone calls and plant visits for that study also had space for data on collection, disposal, and utilization of kiln dust. Later another data form shown in Figure 1 was used for further contacts with cement manufacturers. Data from about 60% of the active cement plants in the United States were processed by computer to provide a basis for estimating the amounts of kiln dust collected, discarded, and utilized by the entire industry.

In addition to contacts with plant personnel for acquisition of operating data, we contacted corporate environmental and managerial personnel of several cement companies, consultants, equipment manufacturers, EPA personnel, potential consumers of waste dust, and suppliers of materials for which kiln dust may be a substitute. These contacts were made to solicit opinions and facts on problems attendant to utilization of dust in particular applications and to seek additional potential applications.

CEMENT KILN-DUST WORKSHEET

SRI ID _____

Company name _____

Plant name and location _____

Contact _____ Ph: _____

1. Kiln-dust collection

a. Collection equipment (check one or more)

Cyclones or multiclones.....☐
Baghouse.....☐
Electrostatic precipitator.....☐
Wet scrubber.....☐
Other (specify).....☐
None.....☐

b. Estimated collection efficiency (%) _____

2. Kiln-dust disposition

a. Total collected (tons/day) _____

Alkali content - K_2O (%) _____
- Na_2O (%) _____
- Na_2O equivalent(%) _____

b. Total returned to kiln (tons/day) _____

Alkali content - K_2O (%) _____
- Na_2O (%) _____
- Na_2O equivalent(%) _____

Method of return

insufflation.....☐
mixed with feed.....☐
leached.....☐

c. Total discarded (tons/day) _____

Alkali content - K_2O (%) _____
- Na_2O (%) _____
- Na_2O equivalent(%) _____

Method of disposal

Surface piling.....☐
Quarry piling.....☐
Slurry to quarry.....☐
Slurry to pond.....☐
Other (describe).....☐
Utilization (describe).....☐

c. Does this company have plans for future utilization
of cement dust? If yes, how? _____

3. Additional remarks (novel practices, special problems, etc)

Figure 1. Sample form used to record survey data.

SECTION IV

THE INDUSTRY

Portland cement is composed of the oxides of calcium, silicon, aluminum, and iron, bound in a complex mineralogical matrix, with the ability to hydrate and harden into a stone-like material. The raw materials generally include a calcium carbonate source such as limestone, cement rock, marl, chalk or oyster shell, a silica source such as sand, quartzite or Fuller's earth, an alumina source such as clay, shale, slag, aluminum ore tailings or fly ash, and an iron source such as iron ore, iron oxide, blast furnace flue dust or iron pyrites.³ Some raw materials contain several of the necessary constituents and thereby reduce the number of materials that must be handled by a manufacturer. The most common combinations of materials are: cement rock; limestone and clay; limestone and shale; and limestone, clay, and iron ore. Naturally occurring raw materials contain unnecessary or undesirable elements such as magnesium, potassium, sodium, sulfur, chloride, fluoride, phosphate, and heavy metals; however, when these are present in only trace amounts, they are not deleterious to the manufacturing process or to the product.

The principal steps in the manufacture of portland cement are quarrying (or dredging of shells), crushing, grinding, blending, firing, and finish grinding. The quarrying and crushing operations are not unique to the cement industry, in fact, almost all mineral quarrying and crushing operations use the same techniques and equipment. Raw grinding of the sized materials reduces them to a fineness of about 200 mesh. Most plants employ ball mills for raw grinding and some add water to the material being ground. Those plants grinding raw material as a water slurry usually keep the material wet until it is dried in the kiln, thus the term "wet process". In those plants grinding raw material dry the term "dry process" has been adopted. Wet process plants pump the ground material to large stirred tanks, called slurry tanks, where the composition is adjusted as necessary and the batch is stirred to assure uniformity. The analogous dry process equipment is a homogenizing or blending silo stirred by introduction of compressed air at the base. Factors that determine whether wet or dry grinding will be used include: moisture content of the raw materials, availability of water, and the price of fuel. (Wet-process plants require additional fuel to evaporate the moisture in the kiln feed.)

Quarrying, crushing, grinding, and blending prepare raw material for the most important step in processing, burning in the kiln. The kiln feed (also called raw meal or raw mix) is continuously metered into the upper end of the kiln to begin its transit of one

to four hours through the kiln. A burner maintains the temperature at the lower end of the kiln at about 1500°C and the feed temperature approaches this value as it traverses the kiln. During the movement of feed through the kiln, three thermally induced events occur: moisture is driven off, the calcium carbonate calcines to calcium oxide, and then the entire mass fuses into semi-liquid, marble-size balls called clinker. The fusion step involves several complex chemical reactions resulting in a new mineralogical material, portland cement clinker.

Clinker discharged from the kiln, usually onto a moving grate clinker cooler, is cooled by a stream of air passing up through the grate. Usually a portion of the hot air from the clinker cooler is used as combustion air for the burner. Water spray cooling is the only other significant clinker cooling method in the industry. After cooling, gypsum (usually about 5% by weight) is added to the clinker to retard hydration. Then the mixture is finely ground (325 mesh) prior to bagging or bulk shipment.

The various standard grades of cement available are all produced with the same equipment and essentially the same raw materials. The differences between cement grades are achieved by variations in kiln operating conditions and ratios of raw materials.

The cement industry is now in a period of growth in production capacity. During the period 1965-70 the cement industry suffered from excess capacity. There were 177 active plants in 1964,¹ and several of these were shut down due to reduced profits and air pollution regulations that required expensive additions of emission control devices. During the 1970's the number of plants has remained in the range of 165 to 170 as new plants come on stream and older plants are closed. However, the larger capacity of newer plants and the expansion of some existing plants resulted in a steady increase of cement shipments in the United States from 75.3 million tons* in 1970 to 87 million tons in 1973.⁴ The value of the 1972 cement shipments was about \$1654 million, producing a profit of about 9% return on net worth.⁵

Locations of portland cement plants are dictated normally by distance to market, availability of transportation and availability of raw materials. Typically, the market area is considered to be within 100-200 miles from the plant along transportation routes. Low cost transportation such as rail or water is usually required to profitably ship cement further than the 10-50 mile radius of the local market. Similarly, proximity of raw materials is imperative if a plant is to compete economically. Most plants utilize

*The cement industry has adopted the short ton, 907 kg, as its standard unit of weight. Therefore, all production figures in this report will be expressed in short tons.

stone quarries adjacent to the plant so that raw material transportation costs are kept low. Some plants, however, are located so as to minimize distribution problems and must transport raw materials several miles from quarry to plant site. Still other plants purchase shell or stone from other suppliers.

The costs of cement production do not depend as much on materials as on labor, which accounts for roughly one-third of the total inplant cost for producing cement. Examples of major costs for 14 plants are given in Table 1.

The future of portland cement is good despite the more stringent pollution control laws. Demand is increasing due to increased construction and increased use of prestressed concrete products. The average annual increase in shipments of portland cement is predicted to be about 3.4%.⁴ Factors which could adversely affect the cement industry are as yet speculative. The greatest threat to the industry is the fuel shortage, which is likely to result in significant process modifications to improve thermal efficiency.

Table 1. PLANT PRODUCTION COSTS
(1973 dollars per short ton)

Plant	A	B	C	D	E	F	G	H	I	J	K	L	M	N	Avg.
Purchased Raw Material	0.69	1.82	1.13	0.76	4.22	5.25	0.76	0.59	0.76	0.85	0.91	4.17	0.65	0.59	1.65
Freight on Limestone			1.06					1.01						1.38	0.25
Waste Dust Disposal		0.16													0.01
Labor	5.85	5.00	6.40	7.23	5.75	4.52	8.40	6.80	7.08	5.48	4.00	3.84	5.59	5.96	5.85
Fuel	2.18	2.39	2.83	2.39	2.39	1.76	3.46	3.40	2.29	1.80	3.09	2.13	2.08	2.66	2.49
Power	1.17	1.92	1.17	1.55	1.86	1.70	1.17	0.75	1.27	1.54	1.59	1.27	1.13	0.75	1.34
Operating and Repair Supplies	1.92	2.07	2.12	2.44	1.92	1.23	1.27	1.75	1.38	1.97	2.44	1.81	2.24	2.92	1.96
Taxes and Insurance	0.37	0.32	0.53	0.21	1.59	0.59	0.11	0.80	0.48	0.64	0.37	0.53	0.32	0.69	0.54
Miscellaneous	0.05	0.05	0.05	0.05	0.50	0.50	0.05	0.05	0.05	0.16	0.05	0.05	0.05	0.05	0.06
Depreciation & Depletion	1.49	2.55	1.59	1.81	1.59	2.39	0.59	1.27	1.59	1.70	1.92	1.59	3.03	1.86	1.78
Total Plant Cost	13.72	16.28	16.86	16.33	19.25	17.45	15.80	16.44	14.89	14.15	14.36	15.37	15.05	16.86	15.91

Source: J.D. Wilson, Bendy Engineering Company, St. Louis, Missouri.

SECTION V

DUST COLLECTION

The Environmental Protection Agency and most state air pollution control agencies have set standards for particulate emissions from cement manufacturing processes. United States Environmental Protection Agency guidelines call for a maximum dust emission from the stack of 0.3 lb of particulates per ton of dry raw feed, and a maximum dust emission from the clinker cooler of 0.1 lb per ton of dry raw feed to the kiln.^{2,6} Because it is almost always relatively coarse and low in alkalies, clinker cooler dust can be collected and returned to the process without any problems. Since clinker cooler dust is seldom discarded it was not covered in this study.

An example of the level of control represented by the EPA guidelines can be demonstrated by the following calculations:

- The average production of a portland cement plant in the United States is about 1670 tons per day.
- Approximately 1.6 tons of raw material are required to produce one ton of clinker resulting in an average feed of about 2672 tons per day.
- The average amount of dust collected (not emitted) is 312 tons per day.
- The average collection efficiency of 101 plants studied is about 96%, so total dust generated is about 325 tons/day.
- The average amount of dust generated per ton of feed is $325/2672$ or 0.122 tons (244 lb) of dust per ton of feed.
- To reduce emission to 0.3 lb of dust per ton of feed, 243.7 lb of dust must be collected which is $(243.7/244) \times 100\%$ or 99.88% removal.

This example is consistent with actual requirements faced by the industry. Most modern dust collection equipment is certified above 98% for normal operating conditions and some collectors have tested as high as 99.98%. The amount of dust that must be removed from exhaust gases depends, naturally, on the total amount of dust in the gases and this can vary tremendously. Dust generation depends on almost every factor that affects cement making. Some of the more noticeable causes of high dust generation are non-uniformity of feed particle size and operation of kilns above the design production rate.

The most important step in preventing air pollution is preventing escape of kiln dust to the atmosphere. To prevent kiln dust escape, many types of collectors have been utilized by cement manufacturers. The types of dust collectors used in the 101 plants surveyed are shown in Table 2.

Table 2. DISTRIBUTION OF KILN DUST COLLECTION SYSTEMS
IN WET AND DRY PROCESS CEMENT PLANTS

<u>Kiln-dust collection system</u>	<u>Type of Process and Number of Plants</u>	
	<u>Wet</u>	<u>Dry</u>
<u>Single dust collector</u>		
Cyclones	2	2
Precipitators	31	3
Baghouses	3	3
Wet scrubbers	1	0
Settling chamber	1	0
<u>Combinations of dust collectors</u>		
Precipitators and wet scrubbers	1	0
Cyclones and wet scrubbers	1	0
Cyclones and precipitators	14	12
Cyclones and baghouses	4	16
Cyclones, baghouses, and precipitators	2	2
Baghouses and precipitators	1	1
Baghouses and wet scrubbers	0	1

The earliest and least expensive dust collector is the settling chamber. A settling chamber is typically a large box in the duct between a kiln and the exhaust stack or chimney. Exhaust gases passing through the chamber experience a reduction in velocity due to the larger cross sectional area of the chamber compared to that of the kiln. Reduced velocity allows large dust particles to settle to the bottom of the chamber. Such "dense" particles are usually 20 to 30% of the dust emanating from a cement kiln. The settled dust is removed from the chamber and usually added to the kiln feed. Only one plant contacted in our survey used a settling chamber as its only dust collector, and this plant is in the process of upgrading its collection system. Although not reported, it is likely that many plants still use settling chambers ahead of more efficient dust collectors.

Cyclones produce better separation results than settling chambers and are utilized extensively in the cement industry. Over half of the plants surveyed use cyclones for kiln dust collection, but only four plants still use them as the only dust collectors. The operating principle of the cyclone is the application of centrifugal force to a moving gas stream by introducing the gas tangentially to the inner surface of a cylinder thus forcing the gas in a circular path. The radial acceleration experienced by the dust particles concentrates them against the wall of the cylinder while gases depleted of dust are removed from along the axis of the cylinder. Both cyclones and settling chambers use a force directed at right angles to the stream flow to remove dust particles but in a cyclone the percentage of dust removed is greater because the radial acceleration is much greater than the acceleration of gravity employed in a settling chamber.

Electrostatic precipitators have been in use in the cement industry for many years. Early installations were generally only slightly better than cyclones but continuing research in construction and materials have made precipitators extremely efficient and have improved economy. The principle of electrostatic precipitation involves the attraction of electrically charged particles to an electrode of opposite charge. As dust laden gas passes through a precipitator, the dust particles are exposed to a corona discharge in an electric field and acquire static electrical charges. Under the influence of the electric field, the charged particles are attracted to electrodes bearing a charge opposite to that imparted to the particles, and are deposited on these electrodes, from which they fall to hoppers below. Usually, electrostatic precipitators comprise two, three, or four stages pneumatically in series.

Electrostatic precipitators are used in 67 of the 101 plants surveyed. As shown in Table 2, they are the preferred dust collector for wet process plants (49 of the 61 plants). The moisture content of the exhaust gases helps in the conditioning of the dust particles that results in electrical conductivity properties of collected dust that are desirable for electrostatic precipitation.

The fabric filters most commonly used to collect cement kiln dust are baghouses. They consist of hundreds of siliconized-glass fabric tubes through which the dust laden gases flow, leaving the dust particles on the inside walls of the vertically hanging bags. The bags are shaken to dislodge the dust which falls into a hopper. The maximum temperature tolerated by the glass bags is somewhat less than 300°C.⁷

Wet scrubbers are employed by only two of the plants in our survey. Only one scrubber is actually used as the primary dust collector, and it has a history of mechanical problems. The dust laden exhaust gases are brought into contact with a high-velocity water spray that entraps the dust particles. The droplets are collected in cyclones and sent to a settling pond. The sludge from the settling pond is usable as kiln feed, but the overflow is a potential water pollution problem.⁸

Combination systems utilizing the best features of two or more collectors are quite common in the cement industry. The most common multiple systems are cyclones with precipitators and cyclones with baghouses. Cyclones are used ahead of the other collectors to remove coarser particles inexpensively and the second system then collects the finer particles. Usually, when alkali problems are encountered with the dust collected in a combination system, only the fine fraction from the final dust collector needs to be discarded.

SECTION VI

CHARACTERISTICS OF KILN DUST

In the process of grinding the raw materials to a fineness of minus 200 mesh, a significant amount of extremely fine particulate matter is produced. When the raw materials are subjected to the tumbling action of the kiln, these fine particles become airborne and are swept away by the hot combustion gases.

Dust collected in an efficient (i.e 98-99.9%) collector shows a wide range of particle sizes depending upon the type and extent of grinding, the type of kiln, and the type of dust collection system employed. The dust sample in Table 3 was extremely fine; most of the particles were less than 6 microns in diameter.⁹ Other studies of particle size analysis reported substantial fractions of the dust with particle sizes as large as 100 microns.¹⁰

Table 3. PARTICLE SIZE ANALYSIS AND DISTRIBUTION OF ALKALIES IN A SPECIMEN KILN DUST FROM AN ELECTROSTATIC PRECIPITATOR⁹

Particle Size Range (Microns)	Weight Percent	Total Alkalies %		Water Soluble Alkalies, %		Water Insoluble K ₂ O, %
		Na ₂ O	K ₂ O	Na ₂ O	K ₂ O	
+68	0	-	-	-	-	-
-68+48	0.3	0.30	3.62	*	*	-
-48+34	0.4	0.31	3.46	*	*	-
-34+24	0.7	0.35	4.51	0.094	1.927	2.58
-24+17	1.8	0.38	5.08	0.117	2.560	2.52
-17+12	5.1	0.40	5.15	0.134	3.072	2.08
-12+6	27.3	0.33	5.35	0.134	3.252	2.10
-6	64.4	0.42	10.72	0.242	8.191	2.53

*Insufficient sample for analysis.

An important factor associated with dust particle size is the distribution of alkalies in the dust. Sodium and potassium sulfates, chlorides, and carbonates exhibit a strong tendency to concentrate in the finer fractions of collected dust because the specific surface area of the particles increases dramatically as effective diameter decreases. This relationship is best shown by the data in Table 3. The relationship of alkali content to surface area is explained by the following sequence of events. First, as the raw materials proceed down the kiln and increase in temperature, sodium and potassium compounds reach their boiling or subliming temperature and vaporize; then, as the gases containing airborne raw material and vaporized alkalies leave the hot part of the kiln, the alkalies

cool and begin to condense both as a fume and onto particles in the gas stream. The fume produced is composed of extremely fine particles and apparently accounts for only a small part of the volatilized alkali. Most of the alkali present in the gases condenses on entrained dust particles, and since the finer particles have more surface per unit of weight to be coated, they contain more alkali per unit of weight, i.e., higher concentration of alkalies than the larger particles.

The chemical composition of kiln dust is determined by the composition of the raw materials and the conditions the dust particles have encountered in the kiln. Published data on the proportions of major constituents, Ca, Mg, Si, K, Na, S, C, etc. vary so widely that no really typical dust composition can be assumed.¹⁰ Careful analysis of a dust sample would reveal a variety of elements, some present in only trace concentrations as shown in Table 4. This particular sample had a high concentration of the usual alkali metals Na and K and smaller concentrations of the others in that group Li, Rb, and Cs.¹¹ Most of the cations are associated with CO₃⁻⁻ and SO₄⁻⁻, but halide anions are also present. Volatile heavy metals such as Zn and Pb are likely to be present in concentrations significantly higher than those found in the raw materials.

The collected kiln dust has experienced some degree of calcination and thus has a lower content of CO₃⁻⁻ than the raw materials. The "loss on ignition" value of the dust may range from 10 to 35% compared to a typical value of about 36% for raw materials. The degree of CO₃⁻⁻ depletion is an indication of how hot the dust became and, therefore, how far down the kiln it traveled before becoming airborne and escaping with the gases. Since the dust is partially calcined it has the ability to harden somewhat upon exposure to moisture.

Table 4. COMPOSITION OF DRIED KILN DUST¹¹

		<u>Weight, %</u>		
Clay (HCl insoluble, fired at 800°)		4.61		
Organic substance		2.06		
<u>Cations</u>		<u>Meq/100 g</u>		
Lithium	Li ⁺	0.0064	0.92	
Sodium	Na ⁺	12.25	523	
Potassium	K ⁺	24.50	627	
Rubidium	Rb ⁺	0.475	5.56	
Cesium	Cs ⁺	0.0074	0.06	
Magnesium	Mg ⁺⁺	Trace		
Calcium	Ca ⁺⁺	9.26	462	
Strontium	Sr ⁺⁺	0.015	0.34	
Sum of Cations		1,618.88		
<u>Anions</u>				
Fluoride	F ⁻	0.46	24.2	
Chloride	Cl ⁻	1.43	40.3	
Bromide	Br ⁻	0.040	0.5	
Iodide	I ⁻	0.0552	0.44	
Carbonate	CO ₃ ⁻⁻	29.59	987	
Sulfate	SO ₄ ⁻⁻	9.06	139	
Sulfide	S ⁻⁻	Trace		
Borate	BO ₃ ⁻⁻	0.152	2.58	
Phosphate	PO ₄ ⁻⁻	Not detectable		
Sum of Anions		1,244.02		
<u>Heavy Metals</u>		<u>Heavy Metal Oxides</u>		
Chromium	Cr	0.011	Cr ₂ O ₃	0.016
Manganese	Mn	0.013	MnO ₂	0.021
Iron	Fe	0.84	Fe ₂ O ₃	1.19
Zinc	Zn	1.62	ZnO	2.02
Lead	Pb	0.562	PbO	0.607
Sum of all determinations			97.825	
Oxygen (from CaO not bound in carbonate)			2.98	
Sum of all constituents			100.805	

SECTION VII

THE ALKALI PROBLEM

The major sources of alkalies in the raw materials for cement manufacture are the argillaceous and siliceous components rather than the limestone or the fuel. Fixed alkali cations in the raw materials are not susceptible to removal by direct water leaching or ion-exchange methods. The only practical way of removing them is through decomposition of the clay structure by heating a lime-clay mix at ratios approaching the formulation of portland cement.¹² Under these conditions changes in mineralogical structure of the clay allow the alkalies to escape as vapors that subsequently condense on the surfaces of cool dust particles in the kiln. When necessary, CaCl_2 can be added to the kiln feed to further volatilize the alkalies.

The alkali content of collected kiln dust is the most important characteristic determining whether the dust can be reused in the manufacture of cement. If the total alkali content of the dust (expressed as Na_2O equivalent) is below about 1%, usually most or all of the dust can be returned to the kiln. Alkalies in the dust upset kiln operation by lowering the fusion temperature of the other materials and thereby increasing the fluidity of the kiln load. This causes a reduction in the thickness of the layer of material coating and protecting the refractory lining of the kiln. Also, the presence of substantial quantities of free alkalies in the kiln material during the burning process results in the formation of free lime, as an equilibrium product.¹³ Moreover, since most of the alkali returned to the kiln eventually finds its way into the clinker, return of high-alkali dust can result in the production of clinker with an alkali content above the limit of 0.6% specified for low-alkali cement. This specification is an effort to avoid problems with the well known "alkali-aggregate reaction".

When the aggregate in concrete contains amorphous silica, alkalies in the cement can react with the silica to cause swelling of the concrete.^{14,15} This slow, insidious deterioration of concrete can be a serious problem in construction of a dam or the foundation of a building, but it would be of no consequence in a sidewalk or driveway. High alkali content of the cement also has an adverse effect on the rate at which concrete gains strength.¹⁶

Many construction contracts and codes routinely specify low-alkali cement, even when non-reactive aggregate is to be used. This trend has forced many cement manufacturers to supply low-alkali cement

when normal cement would be quite adequate. If the manufacturer is fortunate enough to have raw materials with low alkali content he can make low-alkali clinker with no problem. However, if the raw materials contain more alkali than can be tolerated in the clinker, some of the alkali must be removed and discarded. Since alkalies tend to accumulate in the fine dust entrained in the exhaust gases of the kiln, discarding dust is the easiest way to reduce the alkali content of clinker. As dust collection efficiencies for cement kiln effluent gases are improved from the average of 96% presently achieved to the 99.88% required by the New Source Performance Standards, the amount of high-alkali dust collected will increase substantially.

SECTION VIII

DUST DISPOSAL

Kiln dust with a high alkali content or other property making it unsuitable for return to the process is usually discarded. Of the 101 plants surveyed, 16 discard all of the dust they collect, and 57 discard a portion of their dust. The most common method of disposal is piling on plant property. Most often these piles are begun on an unused, fairly level location, convenient to the collection equipment and downwind of the plant proper. Another common practice is to dump the waste dust into an abandoned quarry near the plant. In either case, water pollution problems are encountered due to the solubility of the alkalies in kiln dust. Typically, 30 to 60% of the alkalies present in kiln dust are water soluble and can be leached out as water percolates through the dust piles. The runoff from a dust pile usually has a pH of 12 to 13 and will kill most vegetation. One dust pile containing discarded cyclone dust at least 5 years old produced a leachate solution with a pH of 12.5 while a nearby pile of freshly deposited dust collected in an electrostatic precipitator produced a leachate solution with a pH of 12.9. Thus, the alkalies leached from a dust pile in this instance decreased very little over a period of 5 years. A considerable retention time must be assured before runoff from a dust pile can be released untreated to the environment.

Effluent guidelines for the cement industry require containment of a rainwater runoff from materials storage piles including waste kiln dust piles.¹⁷ In many cases this will require construction of a dike around the dust piles as illustrated in Figure 2. Facilities will be needed for adding acid to obtain a pH in the range of 6 to 9 for the runoff water that percolates through the pile into the containment pond before it is released to the receiving stream. Water slurries of dust occur when wet scrubbers are used for dust collection as in two plants of the 101 surveyed. Another situation resulting in water slurries of dust arises when plants mix dust with water and pump the slurry to a disposal pond or lagoon.¹⁸ Some plants use abandoned quarries as the disposal site for dust-water slurries. Others construct ponds or lagoons where the water slurry can settle, concentrating the suspending solids as a sludge in the lagoon. Most plants that dispose of dust as a slurry use waste water from the plant and discharge the supernatant liquid from the settling pond to surface waters. Naturally, the waste water must be retained or treated before discharge just as rainfall runoff from a dry disposal pile. One alternative to treating water before discharge is to maintain a closed water system by recycling the supernatant liquid back to slurry more dust. In areas where the mean annual evaporation exceeds the rainfall, large evaporation ponds could be used to dispose of alkaline wastewater.

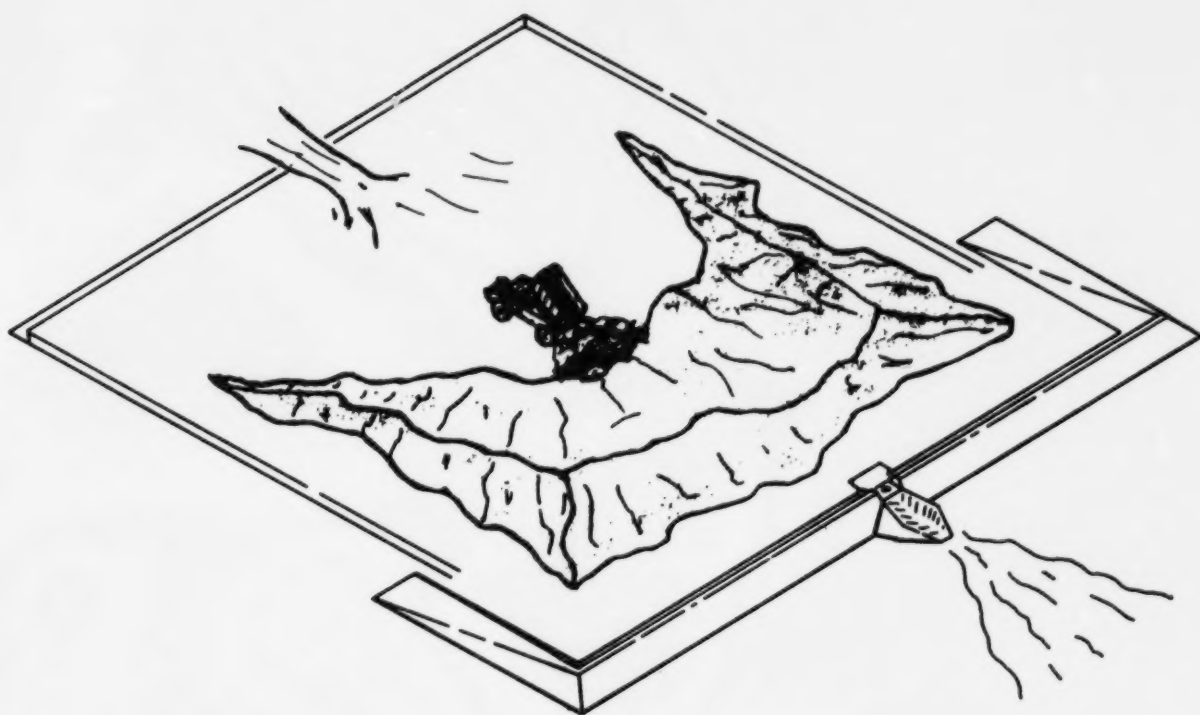


Figure 2. System for containment and treatment of runoff from kiln dust disposal pile.

SECTION IX

DUST RECLAMATION

Presently, 28 out of the 101 plants surveyed return all of the dust they collect to the process, while 16 discard all of the dust they collect. The remainder of the plants, well over half of those surveyed, recycle as much dust as they can without exceeding the limits for alkali content in their clinker, and they waste the remaining dust. On an industry-wide basis, our survey of the amounts of dust collected and discarded indicated that about 73% of the collected dust is reprocessed to make cement. A variety of methods are employed for recycling dust to the kiln. Dust can be introduced to the kiln by insufflation through the burner pipe or a pipe parallel to the burner pipe so that the dust reaches reaction temperature very rapidly.^{19,20} One disadvantage of insufflation is the tendency of the dust to remain airborne due to its fineness, thus establishing a recirculating dust load and wasting energy for collection and reheating. Also, in insufflation the dust cloud in and around the burner causes difficulty in measuring flame temperatures by optical methods.

A second method of dust return employs scoops located about mid-length of the kiln which feed dust from a collar around the kiln to the interior. Scoops appear to be decreasing in popularity as a means of dust return.

Probably the most popular method of dust return to dry process kilns is by blending with the raw feed to obtain a uniform mix so that a more consistent product is obtained. In wet process plants blending of dust with kiln feed is difficult because the partially calcined dust tends to harden when exposed to moisture. Some wet process plants have solved their dust return problems by carefully adding dry dust to the feed slurry just before it enters the kiln. A Russian plant made a slurry of the dust and mixed it with the feed slurry.²¹ Other plants use additives such as molasses or lignosulfonates from pulpwood mills to retard the setting of the dust when it is hydrated.²²

As mentioned previously, most manufacturers discard dust that has too much alkali to allow it to be returned directly to the kiln. The dust has an estimated value of \$2 per ton as a cement raw material because it has already been mined, crushed, and ground. The 4.5 million tons of dust discarded in the United States in 1972 would have been worth \$9 million if it had been used to make cement. Although a variety of methods for reclaiming high alkali dust have been investigated, only one process, leaching, is in use in the United States, and this process is now practiced in only seven plants, six of which are wet-process plants. All of the leaching plants use electrostatic precipitators to collect the dust.

In the leaching process, collected dust is thoroughly mixed with water in a pugmill or mixing tank. This slurry which contains about 10% solids is pumped to a clarifier or thickener where the solids settle to the bottom and excess water overflows.²³ The underflow from the clarifier, a slurry containing about 50% solids is returned to the kiln and burned to clinker. In the single dry-process leaching plant this slurry is injected through a pipe extending down from the feed end of the kiln into a region where the temperature is high enough to flash off the water. In wet process leaching plants the underflow is either mixed with the feed slurry or pumped into the kiln through a pipe parallel to the kiln feed.²⁴

Disposal of the alkaline wastewater from the leaching process is a serious problem faced by cement manufacturers. Two leaching plants discharge their wastes to municipal sewage treatment systems where they claim it is beneficial in neutralizing the acidic wastes in the sewage. Presumably they will be allowed to continue this practice in the foreseeable future. One plant adds acid to the leachate to lower the pH to acceptable levels and one plant carbonates the leachate with stack gas. The other plants discharge the alkaline wastewater directly to rivers, a practice that will be prohibited by the Effluent Limitation Guidelines recently promulgated by the Environmental Protection Agency.¹⁷ By 1977 the levels of pH and suspended solids of the discharge must be controlled, and by 1983 discharge of dissolved solids must be curtailed. This gives manufacturers almost ten years to find a way to recycle leachate or face shutdown of their leaching operations.

The diagram in Figure 3 shows a scheme for eliminating discharge of pollutants from a dust leaching operation. The overflow from the primary clarifier, the water that is now being discharged by most leaching plants, is saturated in lime, has a pH of 13, and contains 10,000 ppm of dissolved solids. In the first carbonator CO_2 from the stack gas reacts with OH^- ions in the leachate to form CO_3^{--} ions. If the alkalinity of the leachate exceeds the hardness, almost all of the calcium is precipitated as CaCO_3 , which has its minimum solubility, 16 ppm, at pH 9.5.²⁵ This precipitate settles to the bottom of the secondary clarifier and is ultimately returned to the kiln. Residual suspended CaCO_3 in the overflow from the secondary clarifier redissolves as the pH decreases in the secondary carbonator.²⁶ This overflow would be within the limits of pH and suspended solids required by 1977.

Electrodialysis appears to be the process of choice to remove alkali salts from the leachate and concentrate them in a solution for recovery of valuable by-products by evaporation and fractional crystallization. The operation of an electrodialysis stack is

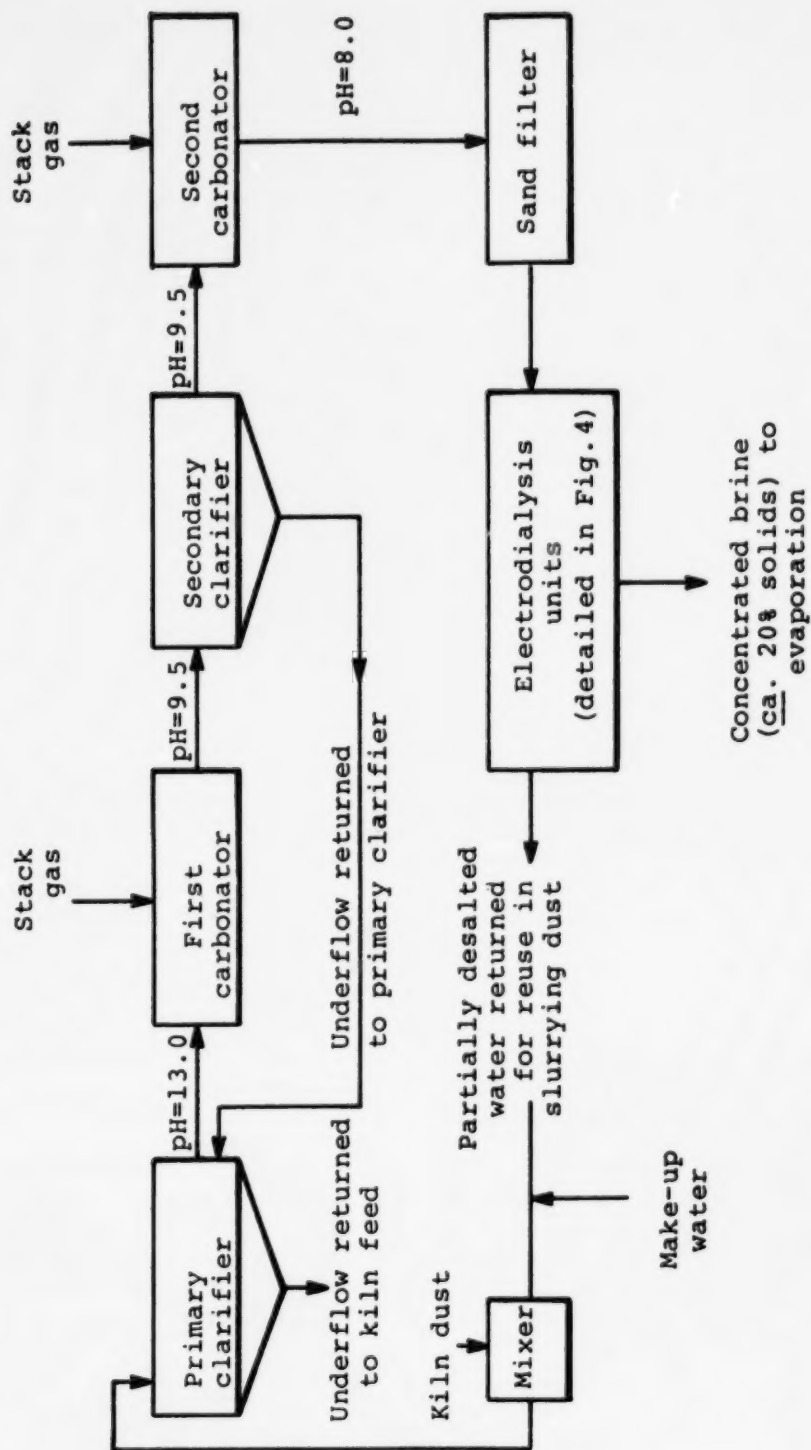


Figure 3. Flow diagram showing steps in electroalytic concentration of leachate.

shown in Figure 4. An electric potential forces ions through semipermeable membranes into a concentrated brine. Water enters the brine by osmosis and carries away the concentrated salts. The partially desalted water is reused to leach alkalies from collected dust, and no water is discharged.

In electrodialysis of water containing appreciable concentrations of calcium, problems are encountered with precipitations of CaSO_4 and CaCO_3 from the concentrated brine. These precipitates damage membranes and block the flow of solutions in the electrodialysis stack. Therefore, it is important that the calcium content of the water be reduced to a very low level by the carbonation procedure described above. Univalent cation-selective membranes that prevent the passage of calcium ions can be used if the alkalinity (OH^- ion content) of a particular leachate is insufficient to allow nearly complete removal of calcium upon carbonation.²⁷ However, this problem would be expected to occur only in plants that use fuel with very high sulfur content.

The concentrated brine from the electrodialysis stack would contain about 20% dissolved solids, mainly K^+ , Na^+ , CO_3^{--} , and SO_4^{--} . Since the ratio of K to Na in the solution is likely to be greater than 10:1, the concentrated leachate may be suitable as a liquid fertilizer. Further purification and concentration of the K, which is the more valuable of the two alkalies, could be achieved by fractional crystallization and evaporation.

Other processes for leaching alkalies from dust have been reported but none is presently being used commercially. During World War I potassium was produced by the Riverside Cement Company.²⁸ CaF_2 was added to the kiln feed to volatilize the K which was subsequently converted to K_2SO_4 in the combustion gases. Collected dust was leached, the leachate was filtered and evaporated, and a precipitate of K_2SO_4 was collected.

A process described in a British patent by Singleton and Bruce utilizes a strong solution of potassium chloride to selectively remove Na from the dust.²⁹ Then K_2SO_4 is removed from the dust by a second extraction. The leached dust is suitable for return to the kiln and the separated K_2SO_4 is a valuable by-product.

Leaching with hot water is reported to be more effective than leaching at ambient conditions. Patzias found that a larger portion of the total alkali in the dust was soluble when the dust-water slurry was heated.^{30,31} Palonen and Kaiser found that high concentrations of alkalies in the leachate could be achieved by countercurrent extraction with hot water.¹³

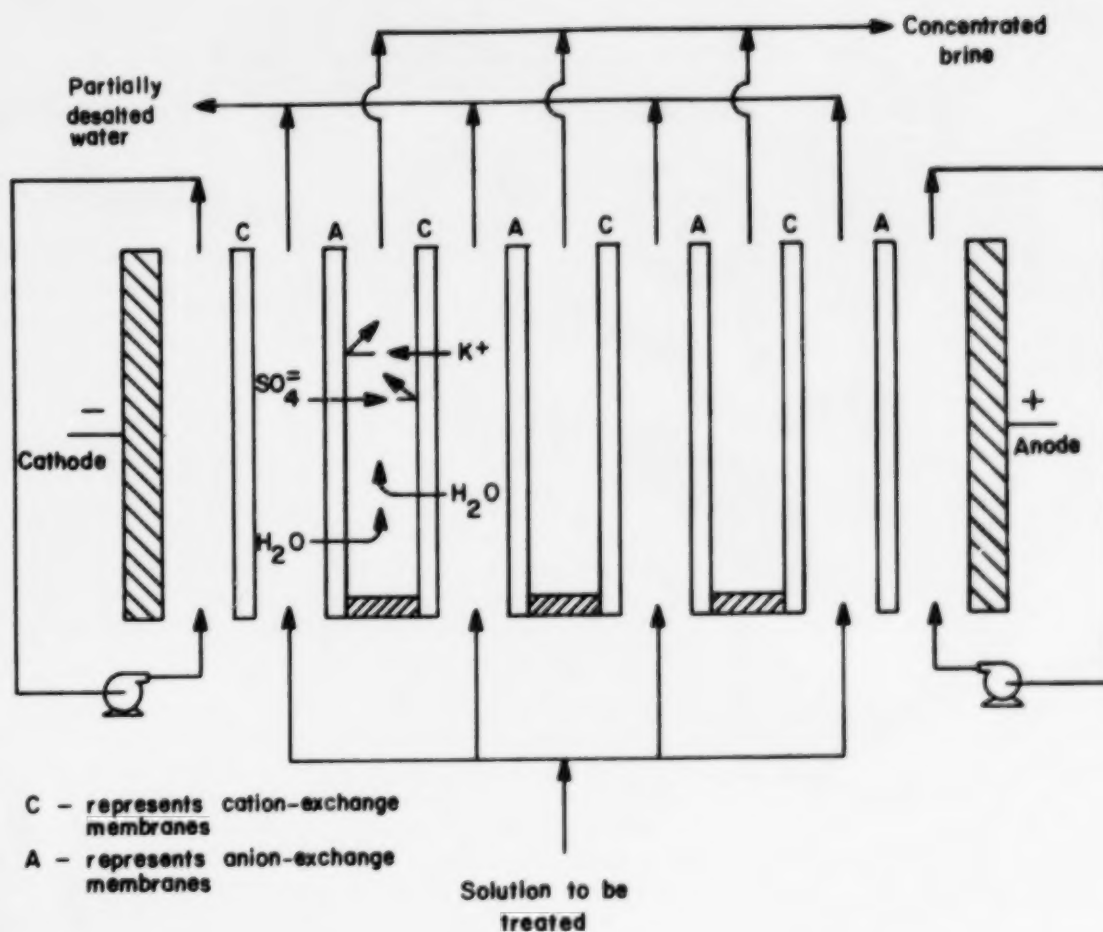


Figure 4. Diagram of electrodialytic concentration stack.

One reason that electrostatic precipitators have found wide acceptance as kiln dust collectors is their ability to separate coarse and fine dust particles. Coarse particles are more easily collected and they tend to predominate in the fraction of dust collected in the first section of the precipitator. The finest particles, which because of their large surface-to-mass ratio have high alkali content, predominate in the fraction of dust collected in the last section of the precipitator. Discarding this fine, high-alkali fraction allows the manufacturer to discard the minimum amount of dust while maintaining acceptably low alkali content in the clinker. Heilmann patented a process in which dust collected in intermediate sections of the precipitator is subjected to further size classification to achieve greater fractionation of alkalis.³²

In a process developed by Bade, hot gases from the kiln with alkalis still in vapor form are cleared of coarse dust particles by a cyclone.³³ Then cool fine dust particles are mixed with the hot gases to condense the alkalis which are subsequently removed with the dust in a second cyclone. Then the hot gases are used to preheat raw materials in a turbulence stack. Cool exhaust gases from the turbulence stack are cleaned by an electrostatic precipitator and the collected dust is recycled to condense alkalis.

A process developed and tested in Russia used cyclone heat exchangers to recover heat and large particles of dust from hot exhaust gases. Then the gases were cooled with finely dispersed water spray to condense the alkalis so they could be subsequently removed in a second dust collector as a powder with 70 to 80% alkali carbonates and sulfates.³⁴

When cement is made in a fluidized bed, the hot exit gases carry away the volatile alkalis. When these gases are cooled either by heat exchangers or by water sprays, the alkalis condense in a form that can be used as a high-grade by-product.^{35,36,37} Fluidized-bed reactors emit very low levels of particulates and they can use low-grade fuels such as kerogen-rich shale. However, since they, unlike rotary kilns, do not employ countercurrent flow of gases and raw materials, expensive heat exchangers are required to achieve reasonable utilization of heat in the system. Figure 5 shows schematically how such a system operates. A fluidized bed pilot plant was operated by the Fuller Company several years ago, but no commercial operation is in existence.

Flame volatilization for alkali recovery utilizes the high temperature of a flame to volatilize the alkalis from the surface of dust particles. The alkali vapors are removed from the hot gases by condensation on a cool surface.⁹ Although flame volatilization actually occurs during insufflation, the alkalis recondense on the dust particles in the kiln, and useful separation of alkalis is not achieved.

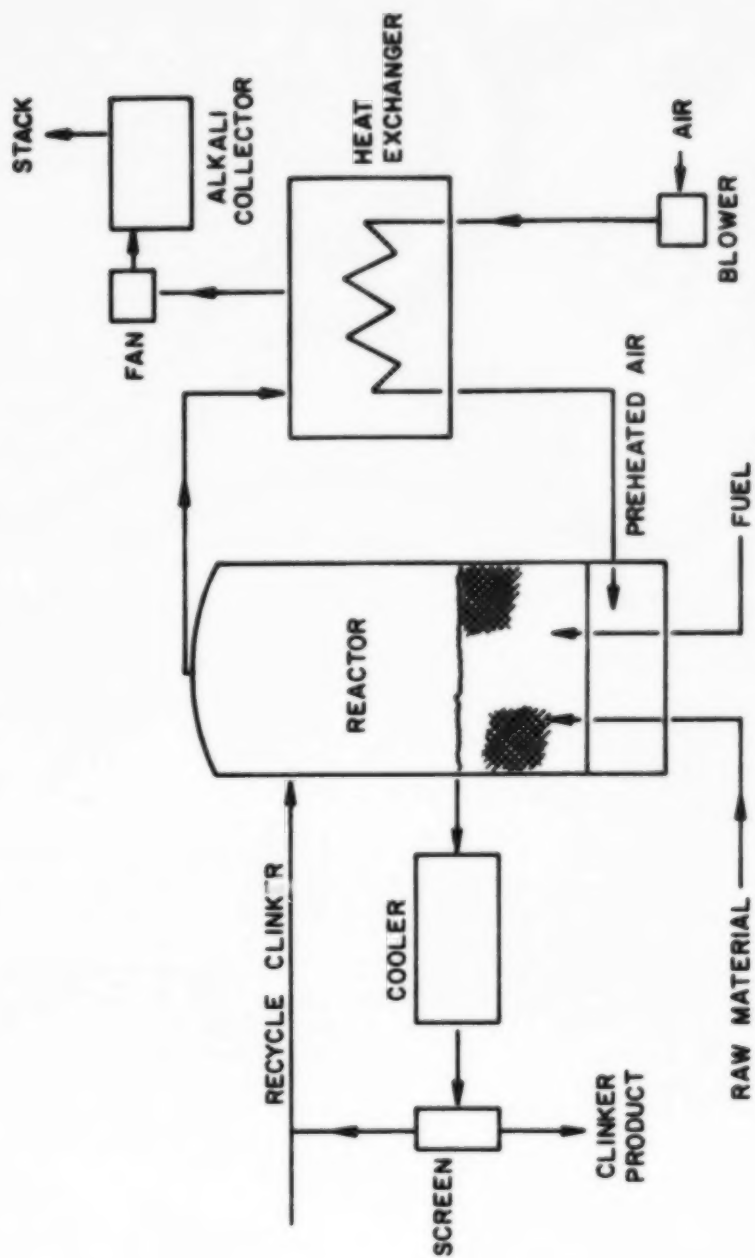


Figure 5. Fuller-Pyzel fluidized bed process for production of clinker and by-product alkalis.

Preheater kilns are commonly used in Europe for fuel economy, and their use is likely to increase in the United States as the fuel shortage worsens. Hot gases from the kiln are brought into direct contact with raw materials in cyclonic-, grate-, or hearth-type preheater. Since alkali vapors in these hot gases will condense on the cool feed materials, preheaters cannot be used with high-alkali raw materials unless the alkalies can be removed from the kiln gases.

Several processes for removing alkalies from preheater kilns are described in the European literature. Polysius developed a process for removing alkali-laden gases from the Lepol preheater collecting the dust, leaching the alkalies, and evaporating the leachate to dryness in a thin film evaporator.³⁸ In a process developed in France, alkalies are condensed from hot kiln gases onto a curtain of moving endless chains.³⁹ The chains are then drawn through a water bath where the alkalies on their surfaces are dissolved and the chains are cooled. In a similar process for removing alkalies from a preheater kiln, the hot, alkali-laden gases pass over cool tubes.⁴⁰ The alkalies that condense on the tube surfaces are scraped off and recovered.

Alkalies can also be removed from preheater kilns via bypass of a portion of the kiln gas that would ordinarily enter the preheater. Nordquist and Heian reported substantial alkali reduction in the clinker produced in a traveling grate preheater (Lepol) kiln when 30% of the 870°C gas was bypassed, cooled to 315°C by mixing with ambient air, cleaned by a cyclone and returned to dry the raw materials.⁴¹ Weber found that considerable alkali reduction could be achieved in a Lepol preheater, but very little alkali was lost from a suspension preheater.⁴² However, his study showed that the alkali content of the clinker could be reduced by adding CaCl_2 to the kiln feed to increase the alkali volatility. Brachthauser patented a process for converting alkalies to the more volatile hydroxide form by vaporizing water in the clinker cooler and blowing this hot moist air into the burner section of the kiln.⁴³

A process for making low alkali clinker from feed materials which may have high alkali content has been patented by Union Carbide.⁴⁴ In this process, the kiln is replaced by a much smaller, stationary, vortex reactor in which clinkering occurs. Alkalies are removed in the gas stream from the clinker reactor. A separate burner and off-gas system are used for suspension preheating the feed prior to clinkering. The process seems particularly useful for converting high alkali dust into clinker and fertilizer.

SECTION X

DUST UTILIZATION

In our survey we found that of the 73 plants that discard some or all of their collected kiln dust, only 13 reported any utilization of the discarded dust. From the figures they reported we estimated that about 1.5% of the 4.5 million tons of waste kiln dust discarded annually is actually being used constructively, and over half of that usage is for landfills. In our review of the literature we found many documented uses of cement dust and in our discussions with industry personnel we received many suggestions for potential uses.

The largest single use of waste dust in the United States is for landfill. In many cases it is difficult to ascertain whether the purpose of the landfill is to dispose of dust or to increase the value of the land. In the former case the cement manufacturer may pay to have his dust hauled to the landfill; whereas, in the latter case he may be able to sell the dust. Both cases were found in our survey. The high temperature when collected and the extreme fineness of the waste dust make it difficult to handle.⁴⁵ Windblown fugitive dust from waste piles or landfills is a significant source of air pollution. Spraying the dust with water is helpful in alleviating this problem.

Some manufacturers employ a rotary unloader like the one shown in Figure 6 to agglomerate the dust before loading it into trucks. The device consists of a rotating inclined drum with water sprays inside. As the hot, dry dust tumbles through the drum it becomes moist and forms nodules that are easy to handle and can be hauled in open trucks to disposal sites. The moisture in the nodules hydrates the cement to some extent so that the nodules do not disintegrate as they dry. Thus, compared to loose dust, the nodulized dust is not as subject to wind erosion or flowing down the pile when it is dumped.

The ability of waste kiln dust to harden after exposure to moisture makes it useful for soil stabilization. One plant in our survey reported that their waste dust was mixed with shells and used as a sub-base for roads. Another reported that they dump their dust in strip mines where it neutralizes acid mine drainage and precipitates iron from the runoff water. Such an application could potentially use large quantities of waste dust.

Kiln dust has also been used as a mineral filler for bituminous paving materials and asphaltic roofing materials. It has also been suggested as a filler for plastics and for asphaltic products

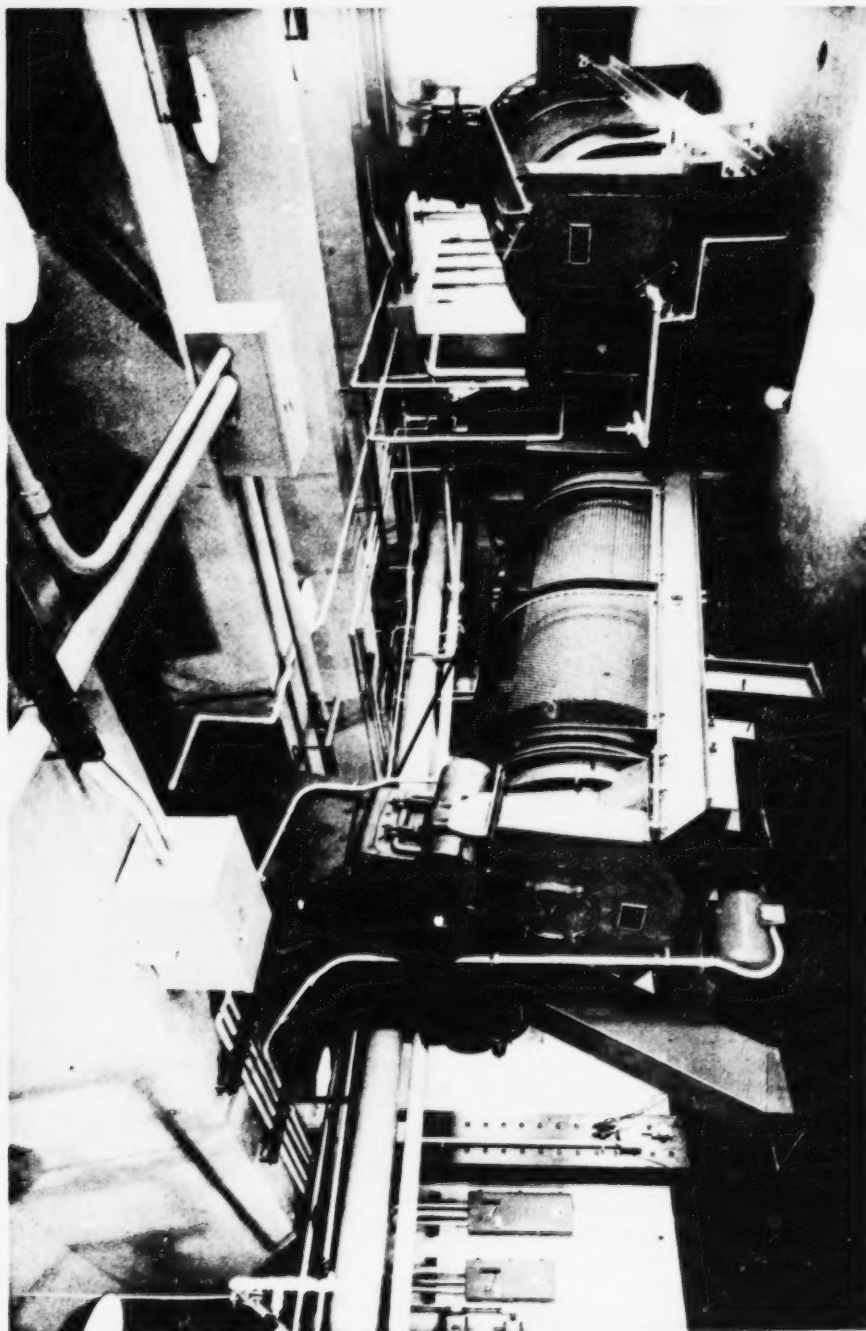


Figure 6. Rotary unloader for nodulizing waste kiln dust
(photograph courtesy of United Conveyor Corp.)

such as insulating board, concrete expansion strips and sound deadening material. There is at least one process under development to use waste kiln dust in the manufacture of lightweight aggregate.

The lime content of the dust makes it useful as a neutralizing agent for acidic bogs, lakes and streams. In a study carried out in 1957, waste kiln dust was used to kill vegetation in an acidic bog.⁴⁶ Considerable interest has been expressed in the possible use of waste kiln dust to treat acid mine drainage. Since fresh dry dust flows so easily, it might be pumped into abandoned mines to neutralize acid, precipitate dissolved iron, and possibly reduce seepage of water from the mine. Industrial acidic wastes that might be neutralized by kiln dust include spent pickle liquor and wastes from leather tanning and cotton seed delinting processes.

Kiln dust has been successfully substituted for lime in coagulation processes. In Oregon, kiln dust was used as a partial and total replacement for lime in the preparation of alum floc for removal of turbidity from water.⁴⁷ The dust successfully neutralized the water and in addition improved flocculation, apparently because the small residual insoluble dust particles provided dense nucleation sites for the alum floc.

In the adsorption of SO_2 from stack gases by wet scrubber slurry, cement kiln dust was found to be better than limestone and almost as good as lime.⁴⁸ Surprisingly, problems of scaling in the scrubber system were less severe with kiln dust than with lime in the slurry.

In the manufacture of glass large amounts of soda are used. Emer found that kiln dust could be used beneficially as a partial replacement for soda in making green glass, because it increased the rate of decomposition of sulfates which is the main cause of foaming in glass baths.⁴⁹ Gregor and Hives reported similar success in the use of kiln dust to make glass where color and high chemical stability are not essential considerations.¹⁰

Agricultural use of kiln dust promises to be a way of converting a waste material into a valuable by-product. Two properties of the dust that make it useful for agricultural purposes are its acid neutralizing capacity and its potassium content. Researchers at the United States Department of Agriculture station at Beltsville, Md., found that cement dust had about 80% of the soil neutralizing capacity of lime and about the same liming qualities as pulverized limestone.^{50, 51} Studies carried out in Latvia showed that cement dust could fully replace lime for treat-

ment of acidic soils to grow sugar beets or corn, and the dust could partially replace lime for growing potatoes and rye.⁵² A study in Hungary indicated that in addition to its stimulation of plant growth, it also had insecticidal properties.⁵³

In Russia and Poland several studies have demonstrated the utility of cement dust application on potato crops. One group found that, whereas most inexpensive potassium fertilizers contain appreciable amounts of chloride which is bad for potatoes, the high alkali fraction of kiln dust had essentially no chloride and was an acceptable, inexpensive substitute fertilizer for potatoes.⁵⁴ Rogalov found that application of cement dust increased the starch content of potato tubers but had no greater effect on the yield of potatoes than other fertilizers.⁵⁵ Litynski explained that the sulfate in kiln dust was responsible for the increased starch content of potatoes fertilized with the dust.⁵⁶ He also suggested that the presence of calcium in fertilizer favorably influenced the uptake of potassium in acidic soils.⁵⁷

A Dutch study indicated that comparable yields of oats were achieved when cement dust or limestone and K_2SO_4 were used for fertilizer.⁵⁸ Litynski found that mixed peas-and-oats crops fertilized with kiln dust contained about 2% more protein than crops grown with KCl fertilizer.⁵⁹ He also found that the dust produced more starch in fodder and more sugar in sugar beets.⁶⁰

The size of the market for agricultural lime and limestone makes it potentially a very good route for disposal of waste kiln dust. More than 20 million tons of lime and limestone are sold each year for agricultural purposes.⁶¹ This single market if properly developed could use most of the 4.5 million tons of kiln dust being discarded in the United States each year. Figure 7 shows the usage of agricultural lime in the United States on a statewide average basis. Also shown are the locations of plants that our survey revealed to be discarding major amounts of dust. Most of these plants appear to be located in or near states where substantial amounts of agricultural lime are used.

Approximately 94% of the potash consumed in the United States is used in fertilizer.⁶² Of the 14 chemical elements essential to plant growth, nitrogen, phosphorus, and potassium are the most rapidly exhausted from the soil and must be replaced by the addition of fertilizers to assure optimum plant growth.^{63,64} Examples of amounts of potassium withdrawn by various crops are presented in Table 5.

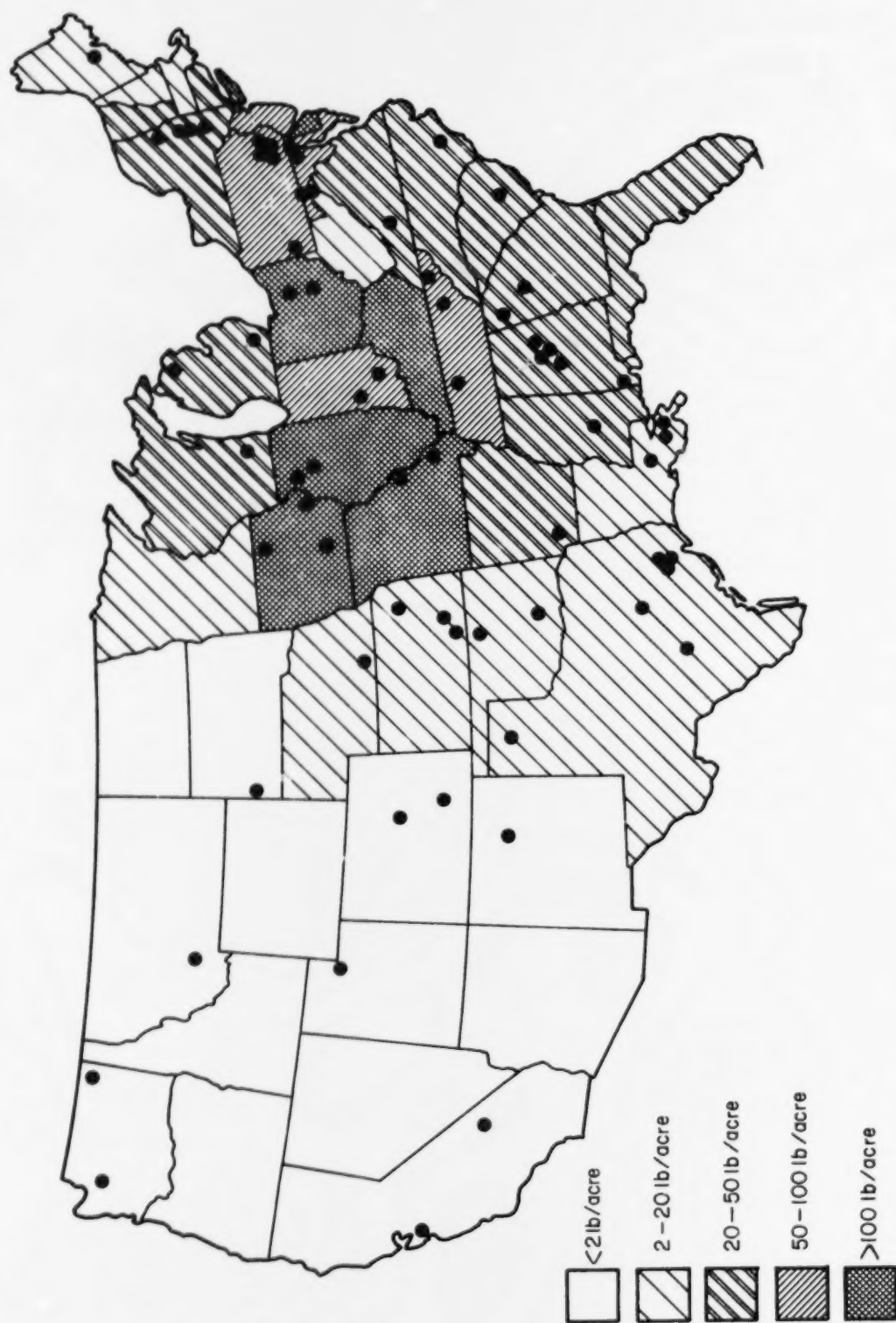


Figure 7. Agricultural lime and limestone usage in the contiguous United States, % and locations of plants known to be discarding kiln dust.

TABLE 5. WITHDRAWAL OF POTASSIUM BY
AGRICULTURAL CROPS^{6,5}

Crop	Good Acre Yield	K ₂ O Removed, lb/acre
Soybean	50 bu	120
Clover grass	9000 lb	175
Peanuts	3000 lb	120
Alfalfa	6 tons	270
Coastal Bermuda grass	10 tons	400
Cabbage	25 tons	210
Irish potatoes	20 tons	310
Tomatoes	30 tons	480
Sugar beets	30 tons	550
Sugar cane	100 tons	590
Rice	4500 lb	110
Corn, ears	150 bu	195
Corn, silage	30 tons	245
Wheat	60 bu	110
Cotton	1250 lb	90
Tobacco	2800 lb	190
Apples	600 bu	135
Peaches	600 bu	120
Grapes	10 tons	80
Oranges	800 boxes	175

Many of the cement manufacturers contacted in our survey reported that local farmers occasionally visit their plants and haul away truck loads of waste kiln dust to spread on their fields. Although the farmers and cement manufacturers alike recognize the value of the dust as a fertilizer material, apparently no great effort has been made to exploit this resource. One hindrance to its exploitation appears to be fertilizer specifications.

Fertilizer is sold on the basis of its nutrient content. The three nutrients mentioned earlier (nitrogen, phosphorus, and potassium) are measured in "units", each unit representing one percent of an available nutrient. A 6-8-4 fertilizer, for example, is guaranteed to contain at least 6 percent of available nitrogen, 8 percent of available phosphoric acid, and 4 percent of available potash (K₂O). There are at least 33 cement plants discarding dust with an average potash content greater than 7 percent. With additions of phosphorus and nitrogen compounds a commercially acceptable fertilizer could be produced using kiln dust without further concentration of the potassium present. Under regulations set by the Alabama Department of Agriculture and Industry, fertilizers offered for sale must meet certain minimum standards for available nutrient

content. There is a regulation which, while not written to cover the sale of cement dust, allows the sale of cement dust without major modifications. Under section 3(b)(1), Act 434, a material which "... contains important quantities of no more than one of the primary plant nutrients (nitrogen, phosphorus, and potassium)" is defined as a "fertilizer material."⁶⁶ Cement dust satisfies this definition if the potassium content is considered. Other regulations which might be met by cement dust are in the areas of a soil-conditioning material and a fortified liming material.

Most of the states adhere to the Uniform State Fertilizer Bill suggested by the Association of American Plant Food Control Officers. This bill cites definitions in the AAPFCO annual publication. Cement dust easily meets fertilizer material definition C-13.⁶⁷ Thus cement dust can meet commercial content requirements.

Once the question of the legality of sale and use of kiln dust for fertilizer is settled, the next question is how can it be applied. One serious problem is the handling of the fine dust. When dry, it flows readily and is easily carried away by the wind. A Russian patent suggests the preparation of granules by rolling the dust in water.⁶⁸ A device like the rotary unloader shown in Figure 6 can be used for this purpose. Then the granules are treated with CO₂ to make them non-hygroscopic and mechanically strong.

If fertilizer markets for kiln dust are developed, it is likely that the manufacturer will want to modify the composition of the fertilizer to meet specific soil and crop needs. Chlorination roasting was used by a Russian group to raise the K₂O content of kiln dust to over 20%.⁶⁹ A Russian patent describes a process in which kiln dust is mixed with a nitric acid-phosphate extract to yield a ternary N-P-K fertilizer.⁷⁰

Fortunately there are abundant supplies of potash in North America so that there is no danger of long-term shortage. However, the potash fertilizer consumption in the United States is over 5 million tons per year,⁶² and there is a general shortage of other fertilizer materials.⁷¹ Cement manufacturers with waste dust problems would be well advised to contact their State Fertilizer Control Officers for a first-hand opinion of the possibilities of using the dust as a fertilizer material.

SECTION XI

LIST OF PUBLICATIONS

1. Davis, T. A., and D. B. Hooks. Utilization of waste kiln Dust from the Cement Industry. In: Proceedings of the Fourth Mineral Waste Utilization Symposium, Aleshin, E. (ed.). Chicago, IIT Research Institute, 1974. p. 354-363.
2. Davis, T. A. Disposal of Waste Dust From Cement Kilns. Record of the 1974 IEEE Cement Industry Technical Conference. Library of Congress Catalog Number 75-28930. IEEE Catalog Number 74CH0785-6 IA.

SECTION XII

APPENDIX

1. Kreichelt T. E., D. A. Kemnitz, and S. T. Cuffe. Atmospheric Emissions From the Manufacture of Portland Cement. Bureau of Disease Prevention and Environmental Control, Cincinnati, Ohio. PHS No. 999-AP-17. 1967.
Abstract: Air pollution control in cement manufacturing was studied in detail. This report gives descriptions of raw materials, processes, equipment, volumes of dust, and methods of dust control employed.
2. Anonymous. Background Information for Proposed New-Source Performance Standards: Portland Cement Plants. NTIS Publication PB-202 459, Technical Report 3, August 1971.
Abstract: Proposed standards for particulate emission of 0.3 lb from the kiln and 0.1 lb from the clinker cooler per ton of kiln feed (dry basis) are justified. The economic impact of the proposed standards is also presented.
3. Anonymous. Concrete Information. Portland Cements (IS 004. 04T), Portland Cement Association, Skokie, Illinois, 1971.
Abstract: Raw materials, processes, types, chemical compositions, physical properties and handling requirements of Portland Cement are discussed.
4. Levine, S. and E. W. Stearn. The Year Ahead--1974. Rock Products, 39-43, December 1973.
Abstract: Construction minerals shipments and values for past years and estimates for 1974 are tabulated. Included is a list of cement plants, capacities, and process types.
5. Grancher, R. A. Cement's Second Look at Capacity. Rock Products. 50-53, 74, December 1973.
Abstract: Cement plant capacity increases, especially in the Southeastern U.S., are forecast through 1978.
6. Anonymous. Standards of Performance for New Stationary Sources. Federal Register 36(159): 15707, August 17, 1971.
Abstract: Standards of performance for portland cement plants are specified for new sources, including plant expansions. Particulate emissions are set at 0.3 lb per ton of feed and 10% opacity (1/2 on Ringleman scale) for the kiln gas effluent. For the clinker cooler these values are 0.1 lb per ton of feed and 1/4 on the Ringleman scale.

7. McCubbin, T. L. Dust Control Techniques for a Portland Cement Plant. Minerals Processing. 24-25, 35, May 1969. Abstract: Generation, composition, and return of kiln dust are discussed. Design and operation of glass-fabric bag collectors are described.
8. Goldberger, R. H. Rx for Cement Dust. Rock Products. 55, 76, 78, August 1973. Abstract: The wet scrubber used for kiln dust collection at National Portland Cement Company's plant in Bethlehem, Pennsylvania, is described in detail. Water that accumulates in the quarry is pumped through venturi scrubbers where it washes out particles of dust from the exit gases of the kilns with 97.7% efficiency. The CO_2 and SO_2 in the gases neutralize the alkalies leached from the dust. The water is then treated in an 80-ft-diameter clarifier where the suspended dust particles are removed for return to the kiln feed. After treatment to oxidize dissolved H_2S , the scrubber water is diluted with quarry water and discharged to a nearby creek.
9. Greening, N. R., R. J. Hinchey, and H. Nagao. Elimination of Water Pollution by Recycling Cement Plant Dust. Progress Report No. 2, Contract No. 802196, Project CR-7050, Basic Research Department, Portland Cement Association, Skokie, Ill., for Office of Research and Monitoring, U. S. Environmental Protection Agency. October 1973. Abstract: A system for flame volatilization of alkalies is described. Particle size analysis, chemical analysis, alkali distribution, and results of experiments are presented.
10. Gregor, M., and L. Hives. Potash Balance of Cement Shaft Kilns with Special Regard to Possibilities of Potash Recovery. Proc. 6th Conf. Silicate Ind., Budapest 1961. 177-89, Pub. (in English) 1963. Abstract: Flue dust samples from shaft kilns at a cement plant were analyzed over a period of 12 weeks. The raw material was lime marl which had a K_2O content of 1.2%. The K_2O content of the flue dust averaged 34%. The quantity of dust collected was 1.7% of the weight of clinker produced. The clinker contained 0.86% K_2O . In addition to its value as an agriculture material, tests showed the flue dust to be a satisfactory substitute for potash in making glass where color and high chemical stability are not essential considerations.

11. Kasz, W. Chemical Investigation of the Dust Collected in an Electrostatic Precipitator at a Portland Cement Plant in Blaubeuren. Jahresber. Mitt. Oberrhein. Geol. Ver. (Stuttgart). 46:1-8, January 12, 1964.
Abstract: The dust was analyzed by chemical methods and x-ray fluorescence spectroscopy, and the composition of the dust was compared with that of the Upper Weissjura marl and chalk, which is the raw material. The dust was enriched in the elements from the raw material that were volatilized in the kiln, specifically, rubidium (0.475% of dust by weight), cesium (0.0074%), iodine (0.0552%), zinc (1.62%), and lead (0.562%).
12. Kester, B. E. Development of Low Alkali Processes in Portland Cement. Preprint No. 63H43, a paper presented at the Annual Meeting of the American Institute of Mining, Metallurgical, and Petroleum Engineers Inc., Dallas, Texas, February 24-28, 1963.
Abstract: The source and nature of alkalies in cement and their effects on certain aggregates are discussed. Leaching systems for wet and dry process plants are described. Steam treatment was studied as a method for destroying hydraulic set properties of dust. The use of CaCl_2 to volatilize alkalies was found to be effective but was more expensive than leaching.
13. Palonen, C. V. and E. W. Kaiser. Inorganic Dust Treatment Process. U. S. Patent No. 2,871,133, January 27, 1959.
Abstract: Kiln dust is pelletized and heated to about 950°C and then leached. The normal 10 to 60% water-soluble content is raised to 94 to 96%.
14. Kryzhanovskaya, I. A., et al. The Effect of Alkalies on the Behavior of Cement. Tsement (Moscow), April 1969. Translation by R. Keen. Cement and Lime Manufacture (London). 97-100, September 1969.
Abstract: Data are presented on cure rates and strengths of cements containing varying amounts of added alkali. The investigations established that, in the presence of 0.6% alkali, the activity of portland cement is reduced irrespective of the kind of alkali compounds present. An increase in the alkali content reduces the activity both at early and late ages due to suppression of the hydration of the clinker materials by the alkalies in the liquid phase.

15. DePuy, G. W. Experiments with Alkali-silica Reactive Constituents of Sand-gravel Aggregate. National Academy of Science - National Research Council, Publ. No. 1367. 41-9, 1966.
Abstract: A pilot study investigated the effect of alkali-silica reactive constituents in a sand-gravel aggregate in the sealed moist-storage and the Conrow cycle mortar bar expansion tests. A highly alkali-silica reactive sand-gravel from the Republican River was tested against South Platte River aggregate as control. It produced deleterious expansion in both the sealed moist-storage test and the Conrow cycle mortar tests. The removal of the alkali-silica reactive particles reduced expansion in the sealed moist-storage test to within safe limits, but in the Conrow cycle test, expansion was reduced but a significant amount of expansion remained. The remaining expansion appeared to be due to the characteristic cement-aggregate reaction of sand-gravel aggregates. The tests indicate that the alkali-silica reaction is a major factor in the cement-aggregate reaction with alkali-silica reactive sand-gravel aggregates. The tests also indicate that the Conrow cycle mortar bar expansion test is sensitive to alkali-silica reaction.
16. McCoy, W. J. and O. L. Eshenour. Significance of Total and Water Soluble Alkali Contents of Portland Cement. Journal of Materials, JMLSA. 3(3):684-45, September 1968.
Abstract: The amount of alkali in cement clinker depends on the raw materials, the burning temperature, and the presence of SO_3 . The ratio of water-soluble to non-soluble alkali can vary from 1:9 to 6:4 (10% to 60%). Relation of Na_2O volatilization to K_2O volatilization: Na_2O volatilizes until about 30% of the K_2O present has volatilized and after that point K_2O volatilizes about 50% faster than Na_2O . Tests reveal that early strengths of cements are higher with some alkali than with none. The amount of soluble alkali has little effect on the pH of aqueous extracts of cement.

17. Anonymous. Effluent Guidelines and Standards - Cement Manufacturing Point Source Category. Federal Register 39(35): 6590, February 20, 1974.
Abstract: Plants in which kiln dust is not contacted with water as an integral part of the process are in the nonleaching subcategory. Effluent limitations (maximum for any one day) for these plants are 0.005 kg of suspended solids per kkg of product, temperature not to exceed 3°C rise above inlet temperature, and pH within the range 6.0 to 9.0. These standards apply to both existing sources and new sources. Plants in which kiln dust is contacted with water (leaching for dust reuse, slurring for dust disposal, and wet scrubbing for dust collection or gas conditioning) are in the leaching subcategory. By 1977 new or existing leaching plants must meet effluent limitations of 0.4 kg suspended solids per kkg of dust leached, temperature not to exceed 3°C rise above inlet temperature, and pH within the range of 6.0 to 9.0. By 1983 leaching plants must meet the same standards as nonleaching plants. For all existing cement manufacturing plants, the runoff of rainfall which derives from the storage of materials, including raw materials, intermediate products, finished products, and waste materials, must meet effluent limitations of 50 mg/l and pH within the range at 6.0 to 9.0 except when the flow exceeds the 10 year, 24 hour rainfall event.
18. Cohrs, F.W. How the Newer Plants Handle Kiln Dust Disposal. Rock Products. 58-59, 80-82, November 1971.
Abstract: An overview is given of dust collection, return and wasting, with results of a questionnaire sent to 30 plants built after 1960 detailing the trend of thinking about dust and the dust handling methods employed. A description is given of the wet dust disposal system at Charlevoix, Michigan, giving the particulars of the system: alkali reduction in the dust, neutralization of the disposal (leachate) water, and suspended solids content of the water (15 ppm). Reuse of the leached and dried dust as a raw material for dry plants is suggested.
19. Rygaard, O. F. Utilization of Cement-kiln Dust. U.S. Patent No. 3,206,526, September 14, 1965.
Abstract: Insufflation of dust as a cloud above the burner pipe avoids obscuring optical pyrometry measurements of flame and clinker. The cloud also helps insulate the upper side of the kiln from radiated heat. Further, a uniform clinker is produced because the dust is mixed with the clinkering mass before its temperature reaches the reaction point.

20. Siegert, L. D. Kilns Reuse Dust the Insufflation Way. Rock Products. 52-54, 81, 84, February 1974.
Abstract: This is a discussion of methods of insufflation of dust and parameters affecting or affected by insufflation, including fuel, flame emissivity, flame propagation, exhaust gas velocity, dust loading, particle size, position of insufflation pipe, and coating of refractories.
21. Dyatlov, I. P. Utilization of Dust Collected in Electrostatic Precipitators. Tsement (Moscow). 28(3):18-19, 1962.
Abstract: The Kuvasaish cement combine in Russia experimented with techniques for returning collected dust to their wet-process kiln. With 97% collection efficiency in an electrostatic precipitator, the dust represented 10 to 20% of the dry mass of kiln feed. Adding dry dust to the feed slurry containing 31-35% moisture resulted in the formation of hard rings that interfered with the movement of the charge through the kiln. The problem was solved by making a slurry of the dust with 45 to 48% water. The dust slurry and the normal slurry were mixed in a scoop slurry feeder and introduced to the kiln via a batch feeder.
22. Dersnah, W. R. and C. F. Clausen. Can That Dust be Used Again? Pit and Quarry. 84-85, 88-91, September 1958.
Abstract: Problems associated with return of dust to wet-process kilns are discussed. Methods of return include hydration and regrinding, leaching, insufflation, and addition via scoops, feed pipes, vortex feeders, and pug mills. Addition of molasses to inhibit hardening is also discussed.
23. Goller, C. H., Jr. Is Dust Leaching Worthwhile? Pit and Quarry, 122-123, August 1966.
Abstract: The four most popular ways to produce low-alkali cement are: use low-alkali raw materials, waste the dust, increase the amount of alkali in the dust and gas, and leach alkalies from the dust to be returned to the kiln. In comparison with the first three ways, the disadvantages of leaching are: higher capital investment, lower reliability, large water consumption, and water pollution.

24. Lindsay, G. C. Don't Throw Away Dust. Rock Products. 65:87-89, 125, July 1962.
Abstract: Missouri Portland's reprocessing of kiln-dust is described. Plant operating advantages are cited: less mud-ring buildup, more uniform product allowing uniform gypsum addition, reduction of alkali sulfate buildup on electrostatic precipitator electrodes, and better control of dust addition to kiln.
25. Quinn, E. L. and C. L. Jones. Carbon Dioxide. American Chemical Society Monograph Series No. 72, 1936. p. 121-125.
Abstract: The action of carbonic acid on calcium compounds, solubility of CaCO_3 in water solutions of CO_2 , and relationship of CO_2 and pH in natural waters are explained.
26. Wilson, J. B. Controls Spark Waste Water Dilemma. Rock Products. 75-76, 92, March 1973.
Abstract: The major water discharges from cement plants are cooling water and water that has been in contact with kiln dust containing soluble alkalies. Leaching of alkalies may occur from runoff of rainwater from waste dust piles, from dust-slurry disposal ponds, or from dust leaching facilities. Leachate may be used to adjust the pH of sewage plants or acid mine drainage. Carbonation of leachate reduces its pH to levels acceptable for discharge.
27. Nishiwaki, T. Concentration of Electrolytes Prior to Evaporation with an Electromembrane Process. In: Industrial Processing with Membranes, Lacey, R. E., and S. Loeb (ed.). New York, Wiley-Interscience, 1972. p. 83-106.
Abstract: This book was written for engineers who wish to determine whether membrane processes should be considered for a given situation and, if so, which process should be used. It also offers theoretical and practical information for the design and operation of membrane processing plants. The use of electrodialysis to recover NaCl from sea water is described in detail. From an initial concentration of 3%, the concentration of salt in the brine is raised to about 20% with an expenditure of about 250 KW-hr per ton of salt concentrated.

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28. Anonymous. Potash from Cement at the Riverside Portland Cement Company. Metallurgical and Chemical Engineering. 16(12):701-703, June 15, 1917.
Abstract: A process to recover 6 lb of K_2SO_4 per bbl of clinker manufactured for each 1% K_2O in the raw mixture (theoretical yield) gave, in fact, 2/3 of this amount. KF is formed when CaF_2 is added to the raw material and the temperature reaches $1100^\circ C$; this is above the KF boiling point and about 90% volatilizes. The combustion gases convert this to K_2SO_4 and the fluoride recombines with calcium in the dust. The dust is leached and the leachate is filtered and evaporated to saturation to precipitate K_2SO_4 . The CaF_2 in the filter cake is returned to the kiln feed.
29. Singleton, F. H. and J. W. Bruce. Improvements relating to the Treatment of Inorganic Dust. British Patent No. 1,131,354, October 23, 1968.
Abstract: A solvent extraction method for removing alkali metals from cement-kiln dust as sulfates and chlorides is described. The process relies on the solubilities of the alkali sulfates and chlorides in various chloride and sulfate solutions. Batch and continuous schemes use compounds recovered in one step to prepare the solvent in the next.
30. Patzias, T. Extraction of Potassium Oxide From Cement Kiln Flue Dust. M.S.C.E. Thesis, Wayne State University, Detroit, Michigan. 1959.
Abstract: Kiln dust is leached with hot water to increase solubility of alkalies. Leached dust is suitable for return to the kiln. K_2SO_4 is recovered from the leachate by crystallization, and the supernatant is recycled to the leaching system.
31. Patzias, T. Recovery of Potassium Sulfate from Cement-kiln Flue Dust. U.S. Patent 2,991,154, July 4, 1961.
Abstract: Cement rotary-kiln flue dusts are leached for extraction and recovery of K_2SO_4 . For example, cement dust is drawn from bins under an electrostatic precipitator and mixed with H_2O in closed tanks. The steam pressure is kept at 150 lb/sq in. absolute, and the extraction is completed in 30 min. The mixture is then filtered, and the solution containing 4.5% K_2SO_4 is evaporated to 19.4%. This solution is neutralized with H_2SO_4 and crystallized. The K salt is centrifuged, and the mother liquor is recycled to the evaporator. When 200 tons of flue dust is extracted with a water-dust ratio of 3:1, 85% of the K_2SO_4 is recovered. The K salts can be worked up for use in fertilizers.

32. Heilmann, T. Treatment of Dust from Cement Kilns. British Patent No. 1,145,827, March 19, 1969.
Abstract: Fractionation of dust in multistage electrostatic precipitators is a method of removing the high-alkali dust for use as a potash fertilizer and returning the coarse, low-alkali dust to the kiln. Data on percentages of potassium, sodium, sulfate and chloride vs particle size are given.
33. Bade, E. Method of and Apparatus for Recovering Substances with a High Alkali Percentage from the Flue Gases of Cement Kilns. U. S. Patent No. 3,288,450, assigned to Polysius G. M. B. H., November 29, 1966.
Abstract: Large particles of dust are recovered from flue gases by cyclones and small particles by an electrostatic precipitator. The large, low-alkali particles collected in the first cyclone are returned directly to the kiln with the feed. The fine precipitator dust is then added to the still hot flue gases where the volatile alkalies condense on the cooler dust particles, increasing their size and weight. The alkali-coated particles are collected in a second cyclone, and the cooler gas with its uncoated dust passes through the precipitator where the dust is collected for recycle to the hot flue gases.
34. Kravchenko, I. V. and I. A. Fridman. Process of Removing Volatile Compounds. Russian Patent 258,906, June 29, 1970.
Abstract: Volatile compounds, e.g., alkalies, are removed from the gaseous effluent of cement kilns by preliminary dedusting followed by cooling with finely dispersed water. The gas stream is cooled to the temperature of condensation of the volatile compounds -- alkali sulfates 900-950°C, carbonates 800-850°C, etc. The consumption of water for removing the volatile alkalies is 0.08-0.09 kg water per kg calcined charge. Full-scale experiments carried out in a dry-process kiln produced a powder containing 70-80% alkali carbonates and sulfates suitable for use in fertilizer.
35. Van Dornick, E. New Cement Process Offers many "Pluses". Rock Products. 57, 89, August 1972.
Abstract: A heat exchanger is proposed to preheat incoming gases above (1100°C), thus preventing condensation of volatilized alkali within the kiln but allowing condensation and recovery from the self-scouring heat exchanger outside the kiln.

36. Van Dornick, E. Will Kilns Give Way to Fluo-Solid Reactors? Rock Products. 116, 138, September 1969.
Abstract: The Fluo-solid reactor is compared with rotary kiln. No specific data are given because of the status of a patent application.
37. Pyzel, R. Hydraulic Cement Process. U.S. Patent No. 3,013,786, December 19, 1961.
Abstract: A process is claimed for production of portland cement by maintaining reaction temperature in a fluidized bed of raw materials in contact with the burning fuel. The fuel can be pulverized coal suspended in the bed, carbonaceous raw materials, or gas mixed with the fluidizing air stream. Advantages claimed include lower capital cost due to smaller equipment necessary, elution of volatilized alkalies away from reacting mass, and small clinker size.
38. Polysius, G. M. B. H. Method of Recovering the Content of Alkali Metal Compounds from Alkali-Rich Dust Obtained when Producing Cement Clinker and Apparatus for Performing the Same. British Patent No. 1,000,984, August 11, 1965.
Abstract: Dust collected from preheater gases at 100 to 300°C is leached with water. The leachate is evaporated in a heat exchanger and dried in a thin film evaporator. Heat for evaporation comes from steam generated by exhaust gases from the clinker cooler. Evaporation is carried out under partial vacuum.
39. Deynat, G. Device for Continuous Extraction of Alkalies from the Escape Gases of a Cement Kiln. U.S. Patent 3,503,187, March 31, 1970.
Abstract: An array of endless chains is exposed to the exhaust gases of a cement kiln, and alkali metal compounds condense on the cool chains. The chains coated with alkalies are revolved out of the gas stream, and the alkalies collected thereon are removed by immersion in a tank of water which dissolves the compounds and cools the chain.
40. Schlauch, R. G. Method for the Production of Hydraulic Cement. U.S. Patent No. 3,043,703, July 10, 1962.
Abstract: A means of condensing alkali vapors on cooled tubes and recovering the alkalies is described. Alkalies in the gases emanating from the reaction zone of a cement kiln condense as a solid on tubes cooled with air or water. The condensed alkalies are scraped from the surfaces of the tubes and collected in a bin.

41. Nordquist, E. A. and G. A. Heian. Alkali Removal via the Grate-kiln System. Rock Products 7th International Cement Industry Seminar. 17-27, 1971.
Abstract: Portions of kiln exhaust gases are cooled to 230°C to solidify gaseous alkalies. Then the warm gases are used to dry the pelletized feed. Alkalies in the clinker and recirculating in the kiln are reduced. Various configurations of the traveling-grate preheater kiln with and without bypass and cooling of portions of gas stream are described.
42. Weber, P. Alkali Problems and Alkali Elimination in Heat-Economizing Dry-Process Kilns. Zement-Kalk-Gips (Wiesbaden, Germany). 17:335-44, August 1964.
Abstract: Investigation of alkali conditions in 11 Lepol kilns and 7 suspension-preheater kilns showed that suspension preheaters allow very little alkali (3 to 19%) to escape from the kiln system into the dust collectors or the atmosphere. Lepol kilns allow more alkali (34 to 100%) to escape so that alkali content of the clinker is lower. Material balance is used to develop an alkali cycle factor that is a function of the volatility and content of raw material alkalies and the amount of residual alkali in the clinker.
43. Brachthausen, K. Process for Producing Substantially Alkali-free Kiln Output when Burning Minerals Containing Difficult-to-volatilize Alkali. U.S. Patent 3,365,521, January 23, 1968.
Abstract: A process is described for converting alkalies to the more volatile hydroxide form by reaction with vaporized water in the kiln.
44. Kiyonaga, K. and P. Wrampe. Method and Apparatus for Producing Cement Clinker. U. S. Patent No. 3,584,848, June 15, 1971.
Abstract: Cement-forming raw materials are introduced into a swirling stream of hot gas in a cylindrical reaction zone where the raw materials react to form clinkers and where the gas stream holds the clinker particles in suspension until the particles grow heavy enough to drop to the lower portion of the reaction zone. Apparatus suitable for carrying out the process is also described.
45. Wolfe, J. M. Kiln Dust - Properties and Handling. Pit and Quarry. 136-7, 140-2, 145, March 1964.
Abstract: Kiln dust is difficult to handle because of its fineness, excessive heat, aeration, stickiness, lumpiness, and alkali content. Flow sheets are presented for a variety of methods for discarding dust or returning it to the kiln.

46. Trembly, F. J., J. A. Mihursky, and E. W. Hertz. Use of Cement Plant Stack Dust as a Neutralizing Agent in Acid Water Lakes. Trans. Northeast Wildlife Conf. 1:55-60, 1958.
Abstract: Cement dust, applied at 40 tons per acre, successfully killed off the acidophilic vegetation in a bog that was to become the bottom of a new lake. A study was begun in 1958 on long term cement kiln dust neutralization of some acidic lakes and ponds in Pennsylvania.
47. Farnham, W. Process of Clarifying Turbid Water Using Cottrell Flour and Acidifying Coagulant. U.S. Patent 2,964,466, December 13, 1960.
Abstract: Kiln-dust from the Oswego plant of Oregon Portland Cement, used as a partial of total replacement for lime as a co-coagulant with alum, improved floc formation so that three test waters were substantially clearer than when treated with alum and lime. The dust successfully neutralized the water to the required range of pH 6.1 to 6.9 and apparently provided floc nucleation sites by virtue of the very small insoluble particles in the dust.
48. Gorman, P. G. Cement Dust as an Absorbent for SO₂ Removal from Stack Gases. Master of Science in Engineering Thesis-Graduate School of University of Missouri. 1972.
Abstract: Cement dust was compared with lime and crushed limestone as a sorbent for SO₂ from stack gases in a wet scrubber slurry. The dust was found to be better than limestone and almost as good as lime for sorption of SO₂ and even better than lime when scaling problems are considered.
49. Emer, P. Formation of Foam on the Surface of Molten Glass Baths. Glastech. Ber. (Frankfurt, Germany). 42:30, June 1969.
Abstract: Kiln dust can serve as a partial replacement for the soda used in glass making. Decomposition of sulfate in the melt is responsible for foaming problems, and the potassium in cement kiln dust accelerates the decomposition, allowing more rapid degassing.
50. C. W. Whittaker, C. J. Erickson, K. S. Love, and D. M. Carroll. Liming Qualities of Three Cement Kiln Flue Dusts and a Limestone in a Greenhouse Comparison. Agronomy Journal. 51:280-2, 1959.
Abstract: Three cement kiln flue dusts had about the same soil liming qualities as pulverized limestone. In cultures all receiving the same total amount of soluble potash, the dusts produced alfalfa yields on initially acid soils equal to or exceeding those produced by the limestone and had similar effects on soil pH, potassium and calcium contents of the crop, and on crop reduction through overliming.

51. Carroll, D. M., C. J. Erickson, and C. W. Whittaker. *Agronomy Journal*. 56:373-76, 1964.
Abstract: Researchers in Beltsville, Md. evaluated kiln dust from 21 cement plants as a substitute for agricultural lime and found that it had about 80% of the soil neutralization power of lime. Kiln dust was found to be superior to crushed limestone for some applications.
52. Bamberg, K. and R. Apenite. *Cement Dust as a Lime Fertilizer*. Tr. Latv. Sel'skokhoz. Akad. (Latvia). 18:151-63, 1967.
Abstract: Cement dust containing 42-47% CaO (of which 44-59% was CaCO₃, the rest Ca silicates), 2.57-2.64% MgO and 1.3% available K₂O was rotary-hoed into acidic soils in the month of May. It was applied at 2-10 tons/ha. and supplemented with lime. If soil with pH above 4.5 was used for neutral-soil plants, e.g., sugar-beets or corn, cement dust could fully replace lime, but for plants growing in slightly more acidic soils, e.g., potatoes or rye, cement dust addition could be 50-60% of total lime.
53. Simakin, A. I. *Agrochemical Properties of Slime Dust of Cement Plants*. Vestn. Sel'skokhoz. Nauk. Ves. Akad. Sel'skokhoz. Nauk (Budapest). 8(5):62-4, 1963.
Abstract: Slime dust of cement plants proved useful as a fertilizer on acidic soils. A typical composition on air-dry basis is N 0.2, P₂O₅ 0.1, and K₂O 15.4%. Trace elements include Mg 1, Mn 0.03, Pb 0.03-0.1, Ag 0.001, Ba 0.01-0.03, Be 0.001, Cr 0.003, Ti 0.1-0.3, V 0.003, Zr 0.001 and Sr 0.1%. It also had insecticidal properties.
54. Kobeleva, E. N., N. N. Popova, and L. G. Shvetsova, *Cement Dust - A Valuable Potassium Fertilizer for Potatoes*. Trudy Sverdlovsk. Sel'skokhoz. Inst. (Sverdlovsk, USSR). 15:59-68, 1969.
Abstract: Cheap potassium fertilizer usually contains an appreciable amount of chloride which can markedly interfere with the development and yield of potatoes, and better grades are too expensive for use on potatoes. The high-alkali fraction of cement dust, which has essentially no chloride, was found to be an inexpensive and acceptable substitute fertilizer.

55. Rogalev, I. E. Improved Forms of Potassium-Cement Dust and its Effect on Potato, Peas, Flax, and some other Crop Yields. *Agrokhimiya* (Moscow). 56-9, January, 1966. Abstract: Three forms of K-cement dust were used to fertilize a heavy loam podzol soil growing potatoes, peas, and flax and a light sandy soil growing corn. The content of K_2O in the three K-cement dusts were 34.9% (in the sulfate form), 40.3% (in the carbonate and sulfate forms), and 41.0% (in a reduced-carbonate and sulfate forms), respectively. It was established that these forms of dusts had no greater effect on yield than ordinary mineral fertilizers. In their effect on the quality of the crops, these K-cement dusts have proven to be superior to KCl. As a result of dust applications, the content of starch in the potato tubers increased 1.3-1.6% compared to results obtained from an application of KCl. The same differences were found for peas (an increase in weight of grains) and flax (an increase in fiber and straw). The intensity of absorption of K in the growth phase from the K-cement dust does not substantially differ from that obtained by the application of ordinary mineral K fertilizers.
56. Litynski, T., K. Mazur, and A. Siekanski. Fertilization of Potato Fields with Cement-kiln Dust. *Zesz. Nauk. Wysszej Szkoły Rolniczej, Krakow, Rolnictwo* (Warsaw, Poland) 5:85-95, 1958. Abstract: Crops of potatoes exactly similar in quantitative respects were obtained by using cement-kiln dust or 40% K salts as a K fertilizer. Starch content in potato tubers was higher in the case of cement-kiln dust. The favorable effect on starch content is probably due to K being present in the sulfate form. Sulfate ions, unlike chloride ions, have a contracting effect on the colloids of the plasma; this causes a rise in starch content of potatoes.
57. Litynski, T., and K. Gorlach. Fertilizing Value of Cement Plant Flue Dust Dependent on Soil Reaction. *Roczniki Nauk Rolniczych, Ser. A.* (Warsaw, Poland). 90 (1):113-30, 1965. Abstract: Two problems were investigated: (1) whether and to what extent the presence of Ca in cement plant flue dust influences its K fertilizing properties, and (2) to what extent the fertilizing value of the flue

dust changes in relation to the pH value of the soil. The experiments were carried out under strictly controlled conditions by a pot culture of sunflower, oats, white mustard, and buckwheat. It has been ascertained that Ca present in cement plant flue dust favorably influences the uptake of K from it, and at the same time it creates more favorable conditions for plant development by reducing the soil acidity. On acidic soils the fertilizing value of flue dust vastly exceeds that of the 40% K salt fertilizer. If however, the pH of the soil is raised by liming, the uptake of K from the flue dust remains practically unchanged while the uptake of K from the K salt fertilizer increases. The reason for this phenomenon may be attributed to different solubility of K in both types of fertilizer and (or) to the antagonism between Ca and K. In general, the raising of the soil pH by liming increases the availability of K in it.

58. Hudig, J., and J. P. Planje. The Cement Dust of the Cement Industry as Fertilizer. *Landbouwkund. Tijdschr.* (Wageningen, Netherlands). 48:593-624, 1936.
Abstract: Comparative yields of oats fertilized with cement dust, CaCO_3 , K_2SO_4 and K_2CO_3 separately and in various combinations are given. The cement dust contained about 4% K in one case and 10% in another. The content of Ca in the form of silicate and carbonate was about 40%. Both Products had about the same effect as combinations of limestone and K_2SO_4 . The cement dust does not add superfluous material to the soil, as most artificial fertilizers do. The authors consider the application of this material as an advantage in cases where K- and Ca- poor soils are to be brought back to profitable production.
59. Litynski, T. Cement-kiln Dusts and their Value for Agriculture. *Zesz. Nuak. Wyzszej Szkoły Rolniczej.* Krakow, Rolnictwo (Wroclaw, Poland). 4:3-27, 1958.
Abstract: Cement-kiln dusts from rotary kilns in the production of portland cement may be an important source of K for plants. The dusts contain approximately 9% K_2O (70% soluble in H_2O , the rest soluble in 2% citric acid) and can be enriched by adding aluminosilicates to the crude mixture. K in these dusts occurs as K_2SO_4 , which by some plants is preferred to KCl. The important other components of the dust are sulfates, CaCO_3 , and colloidal silica. Thus, the dust is a low-percentage K-Ca fertilizer good for acid soils with weak structure. Pot and field experiments showed it equal to, or better than, KCl and 40% K salts as a source of K. Mixed peas-and-oats crops con-

- tained more proteins (about 2% more than crops grown on the latter mixture). The cement dust increased especially the content of starch in potato tubers. It was a good K fertilizer for meadows, where in two experiments protein synthesis was enhanced.
60. Litynski, T. Flue Dusts from Cement Rotary Kilns as Chemical Fertilizers. *Przemysl Chem.* (Warsaw, Poland). 40:260-2, 1961.
Abstract: The potential use of flue dust from cement rotary kilns containing SiO_2 , Al_2O_3 , CaO , and K_2O was investigated in Poland. Potassium compounds in dusts are partly soluble in H_2O and about 80% soluble in 2% citric acid. Field and pot tests showed good fertilizing properties for clinker dusts which contained SiO_2 24.16, CaO 19.94, and K_2O 13.36%. Fertilizing action of this dust compared favorably with that of equivalent quantities of 40% H_2O -soluble standard K fertilizer. It produced more proteins in fodder, starch in potatoes, and sugar in sugar beet roots. Cement dust can be used as chemical fertilizer, preferably in a granulated form as a low grade K fertilizer.
61. Hargett, N. L. 1972 Fertilizer Summary Data. National Fertilizer Development Center, Tennessee Valley Authority, Muscle Shoals, Alabama. 1972.
Abstract: Agricultural materials (limestone, potash, etc) are listed by region and State with consumption from 1950 through 1971.
62. Anonymous. Commodity Data Summaries. Bureau of Mines, Department of Interior. January 1974.
Abstract: Data on production, consumption, and value and forecasts for 95 minerals, metals, and fuels, including cement, lime, potash, phosphate rock and nitrogen compounds.
63. Lodge, F. S. Potash in the Fertilizer Industry. *Ind Eng Chem*, 30:878-882, August 1938.
Abstract: Sources of potash that have been used in the manufacture of fertilizer are described.
64. Rouse, R. D. Potassium Requirements of Crops on Alabama Soils. Bulletin 324, Agricultural Research Station, Auburn University, March 1960.
Abstract: An analysis of 50,000 Alabama soil samples shows that 75% need a fertilizer with equal amounts of P and K and 18% need more K than P. Sources of K are listed and crop requirements of and response to K are discussed.

65. Anonymous. Potassium for Agriculture. American Potash Institute. Revised January 1965.
Abstract: History of potassium in agriculture, function in plants and animals, and relationship to other nutrients are given as introduction. Description of various potassium fertilizer materials, production methods, application methods, and crop responses to potassium are given.
66. Alabama Legislature (Young and Smith), Alabama Fertilizer Law of 1969. Act 434, Regular Session, 1969.
Abstract: This act of the Alabama Legislature sets forth the regulations applicable to the manufacture and sale of fertilizer, fertilizer materials, and other plant food and soil conditioning materials. The regulations follow the recommendations of the Association of American Plant Food Control Officials.
67. Association of American Plant Food Control Officials. Official Publication No.27 Lafayette, Indiana, 1974. p. 37.
Abstract: Officially adopted documents of the Association included in the Uniform State Fertilizer Bill are; Rules and Regulations, Statement of Uniform Interpretation and Policy, Official Fertilizer Terms, and Definitions of Fertilizer Materials. Definition C-13 reads in part, "Waste lime, by-product lime is any industrial waste or by-product containing calcium or calcium and magnesium in forms that will neutralize acids."
68. Dymshits, R. A., N. N. Tikhomirova, E. Ya. Gryazina, E. N. Ostapenko, and L. V. Nelidova. Granular Fertilizers from Cement Dust. Russian Patent 220, 277, June 28, 1968.
Abstract: Granular fertilizers are prepared from cement dust with a high K_2CO_3 content by rolling the dust with an additive of water or a solution of this dust. To prepare non-hygroscopic, mechanically strong granules, the granules are treated with CO_2 or gases containing CO_2 .
69. Nudel'man, B. I., S. Tokhtakhodzhaev, and M. N. Nabiev. Preparation of Quality Standardized Potassium Fertilizers During the Production of a Portland Cement Clinker by Means of Chlorination Roasting. Dokl. Akad. Nauk. Uzb. SSR (Tashkent, 24(10):30-1, 1967.
Abstract: K from the cement kiln charge can be almost fully recovered in the dust collected by electrostatic precipitators when 0.61-1% of NaCl or $CaCl_2$ is added to the charge. K, present in various compounds and minerals, is converted

into KCl by their interaction with the added Cl and sublimed off. The K_2O content of the flue dust of the Kuvasai and Dushanbe plants is thus increased from 6.0 and 7.1 to 13.81 and 20.72%, respectively. The dust can be used efficiently as K_2O - and CaO -bearing raw material by the local fertilizer industry.

70. Tokhtakhodzhaev, S. T., M. N. Nabiev, and B. I. Nudel'man, Process For Manufacturing Fertilizer. Russian Patent No. 176,595, November 17, 1965.
Abstract: The familiar process for manufacturing fertilizer from cement dust consists of recovering the dust obtained from calcining the cement slurry, mixing it with water and neutralizing the alkaline content with phosphoric acid in a mixture of mineral acids. With the goal of manufacturing a fertilizer with a high content of soluble potassium salts, NaCl is added to the cement slurry before it is calcined. The cement dust is recovered in an electrostatic precipitator and mixed with water. The solution obtained is freed from insoluble particles and is mixed with a nitric acid-phosphate extract. The solution may be applied as a liquid ternary N-P-K fertilizer or converted to a solid fertilizer.
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Abstract: Pennzoil's plant in Hanford, Calif. is doubling its production of P_2O_5 to 60 tons/day with plans to produce a 0-50-40 fertilizer by next year. Rising production costs have stimulated the replacement or augmentation of organic and nitrogen fertilizers with potassium-phosphorus fertilizers. Some production costs and material values are given.